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EQUILIBRIUM CONSTANTS FOR IMINE FORMATION FROM ISOBUTYRALDEHYDE AND PRIMARY ALKYLAMINES

A THESIS

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EQUILIBRIUM CONSTANTS FOR IMINE FORMATION FROM

ISOBUTYRALDEHYDE AND PRIMARY ALKYLAMINES

Approv

Chairman

Date approved by Chairman: July 12, 1965

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GLOSSARY OF SYMBOLS

A	Concentration of Aldehyde
a	Debye-Hückel Constant
α	Adjustable Parameter
B	Concentration of Amine
b	Debye Hückel Constant
β	Adjustable Parameter
B_T	Total Concentration of Amine in All Forms
C	Molar Concentration
D	Optical Density
d	Density
ϵ	Extinction Coefficient
E_A	Extinction Coefficient of Aldehyde
E_B	Extinction Coefficient of Amine
E_I	Extinction Coefficient of Imine
I	Concentration of Imine
K	Equilibrium Constant
K'	Equilibrium Constant Involving the Concentration of Water
K_a	Acidity Constant of Ammonium Ion
K_b	Ionization Constant of Amine
K_w	Autoprotolysis Constant of Water in Terms of Molality
K_w^t	Thermodynamic Autoprotolysis Constant of Water
K_w'	Autoprotolysis Constant of Water in Terms of Molarity
l	Cell Length

M	Molarity
m	Molality
p	Concentration of Isobutyric Acid
γ	Activity Coefficient
μ	Ionic Strength in Units of Molarity
W	Molar Concentration of Water

SUMMARY

Although rate and equilibrium in reactions of the type

$$RNH_2 + R'COR'' \rightarrow RN{=}CR'R'' + H_2O$$

have been studied in a number of cases where RNH_2 is a hydroxyamine or hydrazine derivative or where one or more of the R groups are aryl groups, little attention seems to have been given to the simple cases where R, R′ and R″ are all hydrogen or saturated alkyl groups.

Imines and imonium ions are potentially important not only for their possible uses, but also as intermediates in a wide variety of reactions, such as amine-catalyzed aldolization and decarbonylation.

The equilibrium constants for the formation of N-isobutylidene-methylamine, N-isobutylidene-n-propylamine, N-isobutylidene-3-methoxy-proplyamine, and N-isobutylidene-t-butylamine from isobutyraldehyde and corresponding primary amines have been measured. Three methods have been used in this determination, two involving measurements of the ultraviolet spectra and one involving the pH measurements. The ultraviolet measurements are based on the decrease in absorbance at 2850 Å (due to the decrease in concentration of isobutyraldehyde) and the increase in absorbance at about 2300 Å (due to the formation of imines) that occur when increasing concentrations of primary amines are added to aqueous isobutyraldehyde solutions. The pH measurements are based on the fact that the addition of isobutyraldehyde to primary amine buffers decreases the pH values by transforming the amines to

the corresponding imines which are much less basic. For the reaction of methylamine, all three methods were used and found to give within 1.5% of the same value. For the reaction of n-propylamine, 3-methoxypropylamine and t-butylamine, ultraviolet measurements at about 2300 Å and in some cases pH measurements were used, with satisfactory agreement.

The results are given in the following table:

i-PrCH=NR R	Equilibrium Constant U.V. Measurement	pH Measurement	Average
$-CH_3$	91.7 ± 3.5	89.5 ± 2.0	90.7
$-CH_2CH_2CH_3$	76.3 ± 0.7	75.5 ± 1.3	75.9
$-(CH_2)_3OCH_3$	65.2 ± 2.5	63.8 ± 1.5	64.5
$-C(CH_3)$	3.5 ± 0.1	-	3.5

where the equilibrium constants, $K = \frac{[\text{Imine}]}{[\text{Aldehyde}][\text{Amine}]}$, are not involved the concentration of water, since the concentration of water almost remains constant in the equilibrium reaction.

The most significant trend in equilibrium constants noted may be attributed to the steric hindrance.

The autoprotolysis constant of water and the ionization constants of various amines at 35° C and ionic strength other than zero have been calculated from literature and/or determined in this study.

CHAPTER I

INTRODUCTION

Nomenclature of Imines

Imines were discovered by Schiff (1) in 1864. The structure of these materials can be designated as

$$\begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!C{=}N\text{-}R_3 \quad (I)$$

where the R groups may be alkyl groups, aryl groups, or hydrogen atoms.

Compounds with structure I have been referred to as imines, azomethines, anils, or Schiff bases. The nomenclature for compounds of this type is often variable. Chemical Abstracts lists general references to these materials under the categories of imines and Schiff bases. Ketimines refer to compounds where both R_1 and R_2 are alkyl or aryl groups while aldimines refer to compounds where one or both of the groups, R_1 and R_2, is a hydrogen atom. For convenience, the term Schiff bases has been limited to designating those imines where R_1 is an aryl group, R_2 is a hydrogen atom, and R_3 either an alkyl or aryl group (2). Anils are imines in which R_1 and R_2 are an aliphatic group, or an aromatic group, or a hydrogen atom, and R_3 is a phenyl or substituted phenyl group (2). Imines in which R_3 is an alkyl or aryl group are

---

1. H. Schiff, Ann., 131, 118 (1864). (Abbreviations used in these footnotes follow the form employed by Chemical Abstracts.)

2. R. W. Layer, Chem. Rev., 63, 489 (1963).

ordinarily named by Chemical Abstracts as derivatives of the amine R_3NH_2 (3). All the imines discussed in this study which deal with the formation of imines from isobutyraldehyde and primary alkyl amines, are in this category. Therefore, a typical example, $(CH_3)_2CHCH=N-CH_3$, is named N-isobutylidenemethylamine (4). When R_3 is a hydrogen atom, the compound is ordinarily named as an imine; for example, $CH_3CH=N-H$ is named ethylidenimine (3).

Physical Properties

The N-isobutylidenealkylamines studied are all colorless liquids. At room temperature, the densities are in the range 0.7-0.8. The structural refractive constant of C=N is given as 3.75 in Batsanov's scale (5) and 4.04 in Brühl's scale (6).

The ultraviolet absorption spectra associated with the unconjugated C=N system has not been extensively studied. In some cases (7,8) where the alkyl group attached to the imino carbon atom is a primary or secondary alkyl group, the spectra cannot be interpreted unambiguously because enaminisation is possible as follows:

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3. Chem. Abstr., 39, 5928 (1945).

4. Chem. Abstr., 42, 10749 (1948).

5. S. S. Batsanov, Refractometry and Chemical Structure, Consultants Bureau, New York, 1961, p. 41.

6. J. W. Brühl, Z. Physik. Chem., 7, 177, 191 (1891); Ibid., 79, 1 (1912).

7. J. Hires and J. Balog, Acta Univ. Szeged., Acta phys. et Chem., 2, 87 (1956); Chem. Abstr., 51, 15280 (1957).

8. S. F. Mason, Quart. Revs. (London), 15, 316 (1961).

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!CH\text{-}CH{=}N\text{-}R'' \rightleftarrows \begin{matrix} R \\ R' \end{matrix}\!\!>\!C{=}CH\text{-}NH\text{-}R''$$

where R and R′ are alkyl groups or hydrogen atoms, and R″ is an alkyl group.

In 1963, Bonnett and co-workers (9) studied the formation of neopentylidenealkylamines from pivalaldehyde and alkyl amines by ultraviolet measurements in various organic solvents. In this case, enaminisation and aldol-type condensations of the imines are obviated. In hexane solution, λ_{max} for R″=n-Bu, sec-Bu, t-Bu are 244, 243 and 250 mμ respectively and log ε is 1.94, 1.93, and 1.90 respectively. They showed that the wave lengths of maximum absorption and extinction coefficients of neopentylidenealkylamines are dependent on the polarity of the solvent and the alkyl group attached to the imino nitrogen atom. For instance, in ethonolic solution, the λ_{max} of neo-pentylidenebutylamines decreases 7-9 mμ and log ε increases 0.02-0.09 in each case.

A number of N-alkylidenealkylamines give rise to a Raman line near 1670 cm^{-1} (10,11). Cantarel (12) found that simple imines have a Raman line in the same region; he compared their characteristic frequency with those of C=C and C=O, and found it to be closer to the latter:

---

9. R. Bonnett, N. J. David, J. Hamlin and P. Smith, Chem. and Ind., 1836 (1963).

10. A. Kirrmann and P. Laurent, Bull. Soc. Chem., 6, 1657 (1939).

11. L. Kahovec, Acta Phys. Austriaca, 1, 307 (1948); Chem. Abstr. 42, 6665 (1948).

12. R. Cantarel, Compt. rend., 210, 480 (1940); Chem. Abstr., 3592 (1940).

Group	$\Delta\nu cm^{-1}$
C=C	1500
C=N	1670
C=O	1750

The C=N bond distances for several imines have been deduced from the corresponding Raman frequencies by comparison with the C=O distances for several ketones. The average distance for C=O is close to the accepted value of 1.215 Å (13); the imines are considered to be perfectly covalent and a bond distance of 1.24 Å is estimated. Using a carbon double bond radius of 0.665 Å, a nitrogen double bond radius of 0.575 Å may be calculated.

Infrared (IR) absorption due to the stretching vibration of the C=N group in open chain compounds has been assigned to the region 1690-1630 cm^{-1} by Bellamy (14) in 1958. In 1963, Suydam (15) measured the infrared absorption spectra of a series of imines of the type of R-CH=N-R′ where the R and R′ groups are alkyl or phenyl groups. For all of the saturated aliphatic imines (R,R′ = alkyl), Suydam showed that a C=N absorption peak lies within the narrow range between 1664 and 1672 cm^{-1} (5.98 to 6.01 microns), and neither chain length nor branching has any noticeable effect on this frequency.

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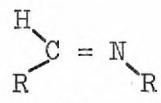
13. L. Pauling, The Nature of the Chemical Bond, 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, p. 224.

14. L. J. Bellamy, Infrared Spectra of Complex Molecules, 2nd ed., Methuen and Co., London, 1958, Chap. 15.

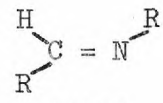
15. F. H. Suydam, Anal. Chem., 35, 193 (1963).

Everard and Sutton (16) report the bond dipole of the C=N bond in aliphatic aldimines to be 1.4 D, which is less than the bond dipoles of 2.5 D for ketones. As the size of the alkyl group attached to the nitrogen is increased, the moment tends to decrease.

Imines possess a double bond, suggesting that geometric isomers should be possible, e.g.



cis



trans

Studies of dipole moment (16) and Raman spectra (12) indicate that aldimines exist very largely at least in the trans form. Other studies have been made and confirmed that no isomerization occurred and all the aldimines exist in the trans form. (7,17).

If aldimines exist only in the trans form, it will not be necessary to correct for the presence of some cis isomer in evaluating the carbon-nitrogen double bond dipole. This bond dipole may be compared with those of C-N (0.45 D) and C≡N (3.2 D from solution measurements and 3.6 D from gas measurements). The dipole of carbon-nitrogen bonds evidently do not rise linearly with the multiplicity as do the energies (18). On the contrary, the difference between the triple and the double

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16. K. B. Everard and L. E. Sutton, J. Chem. Soc., 2318 (1948).

17. V. DeGaouck and R. J. W. LeFevre, J. Chem. Soc., 741 (1938).

18. L. Pauling, The Nature of the Chemical Bond, 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, pp. 85, 189.

bond dipoles markedly exceeds that between the double and the single bond dipoles.

Coates and Sutton (19) studied the bond energy of C=N by burning N-isobutylidene-n-butylamine and on the basis of heat of atomization of graphite and nitrogen.

$$C(s) \rightarrow C(g)\ (^3P) \qquad -126.3 \text{ kcals/mole}$$

$$N_2(g) \rightarrow 2N\ (g) \qquad -170.2 \text{ kcals/mole}$$

The bond energy, 137.5-147.5 kcal/mole was obtained. In 1962, Bedford and co-workers (20) burned the same compound and obtained the value 142.6 kcal/mole.

All the imines whose ionization constants have been determined have been found to be more weakly basic than the primary amines from which they are derived. Cordes and Jencks (21) measured the ionization constants of a number of substituted N-benzylidene-t-butylamines. They observed values ranging from 5×10^{-7} for the p-methoxy compound to 2.5×10^{-9} for the p-nitro compound. Březina and Zuman (22) reported that the ionization constants for the ketimines derived from methylamine and cyclohexanone and cyclopentane are 3×10^{-5} and less than 10^{-6}, respectively.

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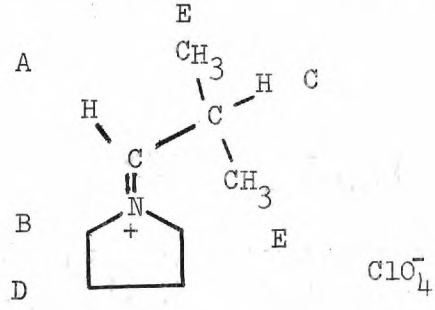
19. G. E. Coates and L. E. Sutton, J. Chem. Soc., 1187 (1948).

20. A. F. Bedford, P. B. Edmondson and C. T. Mortimer, J. Chem. Soc., 2927 (1962).

21. E. H. Cordes and W. P. Jencks, J. Am. Chem. Soc., 85, 2843 (1963).

22. M. Březina and P. Zuman, Chem. Listy, 47, 975 (1953); Chem. Abstr., 48, 5674i (1954).

The nuclear magnetic resonance spectrum of N,N′-dipiperonylidene-ethylenediamine has been studied (23). The band position of the hydrogen atom attached to the imino carbon has been assigned to 8.17 p.p.m. downfield from the tetramethylsilane. Leonard and Paukstelis (24) reported the spectrum of N-isobutylidenepyrrolidinium perchlorate. The signals occurred at 8.35 p.p.m. (J=9.0 c.p.s. doublet) (A), 4.16 p.p.m. (B), 2.97 p.p.m. (C), 2.23 p.p.m. (D), and 1.31 p.p.m. (J = 7.0 c.p.s., doublet) (E). The assignments were made as shown



In this ion the A proton was shown to be coupled to the C proton (J_{AC} = 9.0 c.p.s.) and to the B proton (J_{AB} = 2.0 c.p.s.). The magnitude of J for spin-spin coupling through three single bonds and the $C{=}\overset{\oplus}{N}$ double bond is in the range observed for long-range coupling in the system $H\!-\!C{=}C\!-\!C\!-\!H$ (25). The coupling of the C proton to the E protons gave a doublet with J_{CE} = 7.0 c.p.s.

Recently, Bonnett (26) studied the nuclear magnetic resonance

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23. N. S. Bhacca, D. P. Hollis, W. F. Johnson and E. A. Pier, High Resolution Nuclear Magnetic Resonance Spectra Catalog, Vol. 2, Varian Associates, Palo Alto, California, 1963, No. 673.

24. N. J. Leonard and J. V. Paukstelis, J. Org. Chem. 28, 3021 (1963).

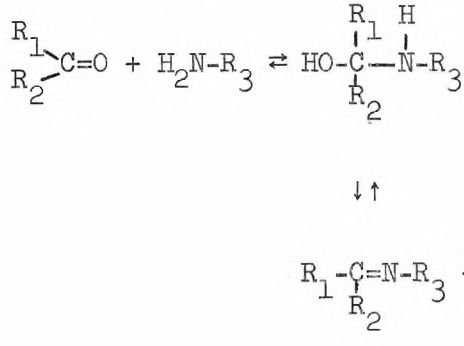
25. J. R. Dyer, Applications of Absorption Spectroscopy of Organic Compounds, Prentice-Hall, Inc., N.J. 1965, p. 99.

26. R. Bonnett, J. Chem. Soc., 2313 (1965).

spectra of N-neopentylidenealkylamines and showed that the band for the proton attached to the imino carbon appears at 7.41-7.50 p.p.m. This signal appears to be weakly coupled ($J \sim 1.5$ c.p.s.) to the proton attached to the carbon atom adjacent to nitrogen.

Formation of Imines

There are several methods for preparing imines (27-32), of which the most common is the reaction of aldehydes or ketones with amines. Only this method is of interest in this thesis, which deals with the equilibria between isobutyraldehyde, alkylamines and corresponding N-isobutylidenealkylamines. This reaction was discovered by Schiff (1). The general equation can be expressed as



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27. C. Moureu and G. Mignonac, Compt. rend., 156, 1801 (1913); Chem. Abstr., 3114 (1913).

28. M. Busch and F. Falco, Ber., 2557 (1910).

29. J. J. Ritter, J. Am. Chem. Soc., 55, 3322 (1953).

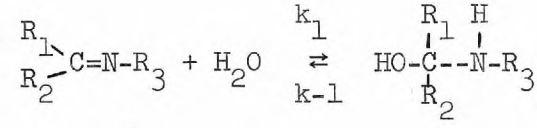
30. F. Barrow and F. J. Thorneycraft, J. Chem. Soc., 769 (1939).

31. K. Hoesch, Ber., 48, 1122 (1915); ibid., 50, 462 (1917).

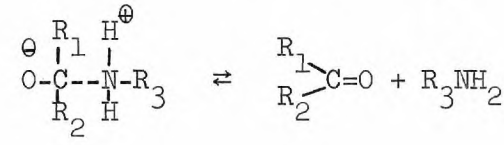
32. E. C. Britton, and F. Bryner, U. S. Patent 1,938,890; Chem. Abstr., 42, 7744 (1948).

Studies of rates and equilibria have been studied in a number of reactions of this type, but have been largely limited to those cases where R_3NH_2 is a hydroxylamine, semicarbazide, or hydrazine derivative. Little attention seems to have been given to the cases where the R's groups in I are all hydrogen and/or saturated alkyl groups.

The formation and hydrolysis of a number of oximes, semicarbazones, and related compounds has been shown to proceed through Equation A and B, with step A rate-determining at neutral and alkaline pH values and step B rate-determining at acidic pH values (33,34).



(A)



(B)

Morton and Pitt (35) have shown that the rate of retinylidenemethylamine hydrolysis is much slower in acid than in neutral solution and this behavior has been interpreted in terms of a change in rate-determining step from A to B at low pH values. Crowell and McLeod (36)

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33. E. H. Cordes and W. P. Jencks, J. Am. Chem. Soc., 85, 2843 (1963).

34. W. P. Jencks., Progress in Physical Organic Chemistry, Vol. 2, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Eds., Interscience Publishers, New York, N.Y., 1964, Chapter 2.

35. R. A. Morton and G. A. J. Pitt, Biochem. J., 59, 128 (1955).

36. R. K. McLeod and T. I. Crowell, J. Org. Chem., 26, 1084 (1961).

found that the condensation of primary amines with aromatic aldehydes in methanol proceeds at a rate proportional to the concentrations of the un-ionized reactants and is subject to general acid catalysis by acetic acid. In 1963 Cordes and Jencks (33) studied the rates of hydrolysis of a series of substituted N-benzylidene-t-butylamines and found that it followed Equations A and B in the pH range 0-14 at 25°. The compounds studied are fairly closely related to the imines discussed in this thesis. However, additional work would be desirable to tell whether this mechanism holds in the reaction of aliphatic carbonyl compounds with primary alkylamines.

The most practical and widely adopted method for the synthesis of aldimines (37) is a modification of the one described by Chancel (38). The reaction is carried out by adding the aldehyde to the amine without a solvent at 0°. After the addition is complete, solid potassium hydroxide is added to remove the water formed in the reaction. Finally, the aldimine is distilled from potassium hydroxide. The N-isobutylidene-alkylamines obtained in this work were water white when freshly distilled, but are unstable and polymerize on standing. They should be stored under nitrogen in a refrigerator and, for some purposes, used within a few hours after distillation.

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37. K. N. Campbell, A. H. Sommers, and B. K. Campbell, J. Am. Chem. Soc., 66, 82 (1944).

38. M. F. Chancel, Bull. Soc. Chim. France, 11, 933 (1894).

CHAPTER II

PRINCIPLES OF OBTAINING EQUILIBRIUM CONSTANTS

pH Measurements

If isobutyraldehyde is added to an aqueous solution of an amine, the following equilibrium will be established

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CHCHO + RNH_2 \rightleftarrows \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CHCH{=}N\text{-}R + H_2O$$

with some of the amine being used to form the corresponding N-isobutylidenealkylamine, which is a much weaker base. Thus, the addition of the aldehyde will cause the pH to decrease. A relationship between the pH, the concentrations of the reactants and various equilibrium constants may be derived as follows.

First, consider the dissociation of amine

$$RNH_2 + H_2O \rightleftarrows RNH_3^+ + OH^-$$

$$K_b = \frac{[BH^+][OH^-]}{[B]} \qquad (1)$$

where K_b is the dissociation constant of amine and $[B]$, $[BH^+]$ and $[OH^-]$ are the concentrations of free amine, ammonium ion and hydroxide ion, respectively.

Before addition of aldehyde, the concentration of hydroxide ion can be obtained from Equation (1).

$$[OH^-]_o = \frac{K_b^o[B]_o}{[BH^+]_o} \qquad (2)$$

the subscript (or superscript) zero represents the dissociation constant of amine and the concentration of each species under the initial concentrations.

Similarly, after addition of aldehyde the concentration of hydroxide ion can be written as

$$[OH^-]_f = \frac{K_b^f[B]_f}{[BH^+]_f} \qquad (3)$$

where the subscript (or superscript) f represents the dissociation constant of amine and the concentration of each species under the final conditions.

From Equations (2) and (3) the ratio of the concentration of hydroxide ions is obtained.

$$\frac{[OH^-]_o}{[OH^-]_f} = \frac{K_b^o[BH^+]_f[B]_o}{K_b^f[B]_f[BH^+]_o} \qquad (4)$$

An alkylamine-alkylammonium buffer solution is used instead of plain aqueous amine solution. The alkylammonium ion in Equation (4) comes from two sources: from the alkylammonium salt that was produced by the addition of strong acid such as perchloric acid or hydrochloric acid, and from the dissociation of alkylamine.

Isobutyaldehyde is easily oxidized to isobutyric acid. The concentration of aldehyde solution should be corrected for the acid formed from it. It is also important to neutralize the free acid before adding

the aldehyde to the amine solution. In these measurements, the isobutyric acid was neutralized by standard sodium hydroxide solution until a pale-green color appeared for the indicator bromothymol blue.

During the addition of aqueous isobutyraldehyde, the concentration of alkylamine and alkylammonium ions decreases. Therefore, the ionic strength changes significantly, and changes in the ratio, $\frac{K_b^o}{K_b^f}$, in Equation (4) are not negligible.

From Equation (4), using the pH value of the alkylamine-alkylammonium buffer solution before addition of aldehyde and the ionization constant of water at the given ionic strength and temperature, the value $[OH^-]_o$ can be calculated; from the amount of strong acid added, the concentration of alkylammonium ion can be obtained from the fact that the solution must be electrically neutral. Since the hydrogen ion concentration is never larger than 10^{-10} M, electroneutrality requires that

$$[BH^+] = [OH^-] + [X^-] \tag{5}$$

where $[X^-]$ is the concentration of the anion of the strong acid used to make the buffer solution.

The ionic strength of the solution after each stepwise addition of isobutyraldehyde can be calculated from the equation

$$\mu = \Sigma \frac{1}{2} C_i Z_i^2 \tag{6}$$

where C_i is the molarity of the ionic species i whose electric charge is Z. The summation indicated is carried out over all ionic species in solution.

The values of K_b at different ionic strengths are obtainable by a method that will be discussed in the next chapter.

The amount of N-isobutylidenealkylamine formed when the equilibrium is established, is simply equal to the difference between the sum of the concentrations of alkylamine and alkylammonium ion and the sum of the concentrations of alkylamine and alkylammonium ion that would be present if the sole effect of the addition of the aqueous aldehyde solution were dilution, i.e.,

$$[I] = \{[BH^+]_o + [B]_o\} \times \frac{V_o}{V_o+V} - \{[BH^+]_f + [B]_f\} \qquad (7)$$

where [I] is the imine concentration, V_o is the volume of alkylamine-alkylammonium buffer at the original concentration and V is the volume if isobutyraldehyde solution added.

The final concentration of isobutyraldehyde may be calculated from the volume of standard aldehyde solution added and the concentration of imine formed.

The equilibrium constant for imine formation can be obtained by substituting the concentration of imine [I], alkylamine [B], and isobutyraldehyde [A] into the expression,

$$K = \frac{[I]}{[A][B]} \qquad (8)$$

which is applicable under conditions where the concentration of water remains essentially constant.

Ultraviolet Measurements

When saturated primary amines are added to aqueous solutions of isobutyraldehyde the absorbance at 2850 Å, due to the aldehyde, decreases, and the absorbance at about 2300 Å, due to the imine, increases. By quantitative measurements on the ultraviolet spectra of aqueous solutions of aldehyde and amine, or of imine, the equilibrium constant for the formation of the imine may be determined. The fundamental relationship used in this determination is the Beer-Lambert Law (39-41), according to which

$$D = \epsilon c l$$

where D is the optical density, ϵ is the molar extinction coefficient, c is the molar concentration, and l is the path length (or cell length), which will be expressed in centimeters in the present work.

The equation for the reaction equilibrium is

$$(CH_3)_2CHCHO + RNH_2 \rightleftarrows (CH_3)_2CHCH{=}N\text{-}R + H_2O$$

This equilibrium can be approached from either side; first, mixing the aldehyde and amine solutions; second, hydrolyzing the N-isobutylidenealkylamine. Both methods have been tried, but the latter has the disadvantage of the instability of imines.

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39. J. R. Dyer, Applications of Absorption Spectroscopy of Organic Compounds, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1965, p.9.

40. H. H. Jaffe and M. Orchin, Theory and Applications of Ultraviolet Spectroscopy, John Wiley and Sons, N.Y., 1958, p. 8.

41. A. Beer, Ann. Physik., 86, 78 (1852).

Define.

D: Optical density of solution.

I: Equilibrium concentration of imine.

A: Equilibrium concentration of aldehyde.

A_o: A + I.

B: Equilibrium concentration of amine.

B_o: B + I.

B_T: The total concentration of amine in all forms, which is equal to B + I + BH^+ or B_o + BH^+.

E_A: Extinction coefficient of aldehyde.

E_B: Extinction coefficient of amine.

E_I: Extinction coefficient of imine.

W: Concentration of water.

The equilibrium constant for imine formation has been expressed in Equation (8). The optical density of the equilibrium mixture is the sum of the contributions of the components present in the solution, namely, the aldehyde, amine, imine, and ammonium ion. Therefore, with a cell length of 1.00 cm,

$$D = AE_A + BE_B + IE_I \tag{9}$$

since the absorption of ammonium ion is negligible.

The final concentration of aldehyde is equal to the difference between A_o, which is the concentration of aldehyde that would be present if none had reacted to give imine, and the concentration of imine.

$$A = A_o - I \tag{10}$$

The final concentration of amine is

$$B = B_o - I \tag{11}$$

substituting Equation (10) into Equation (8),

$$I = \frac{KA_oB}{1 + KB} \tag{12}$$

substituting Equation (10, (11), and (12) into Equation (9),

$$D - A_oE_A - B_oE_B = \frac{KA_o(E_I - E_A - E_B)}{1 + KB} \tag{13}$$

Equation (13) may be rearranged to give

$$\frac{A_o}{A_oE_A + B_oE_B - D} = \frac{1}{E_A + E_B - E_I} + \frac{1}{KB(E_A + E_B - E_I)} \tag{14}$$

Equation (14) is used for measurements of absorbance at the absorption maximum of the aldehyde, where the absorption due to amine and imine are small and the optical density at equilibrium is less than the product of the original concentration of aldehyde and its extinction coefficient.

If measurements are made at the absorption maximum of the imine, where the absorption due to aldehyde is small, the following modification of Equation (14) is used in order to deal with positive numbers.

$$\frac{A_o}{D - A_oE_A - B_oE_B} = \frac{1}{E_I - E_A - E_B} + \frac{1}{KB(E_I - E_A - E_B)} \tag{15}$$

If we define

$$K' = \frac{I.W}{A.B} ,$$

then,

$$K = \frac{K'}{W}$$

Equation (14) and (15) would change to (14′) and (15′) respectively.

$$\frac{A_o}{A_oE_A + B_oE_B - D} = \frac{1}{E_A + E_B - E_I} + \frac{W}{K'B(E_A + E_B - E_I)} \qquad (14')$$

$$\frac{A_o}{D - A_oE_A - B_oE_B} = \frac{1}{E_I - E_A - E_B} + \frac{W}{K'B(E_I - E_A - E_B)} \qquad (15')$$

Measurements at the absorption maximum of the imine has the advantage of utilizing the extinction coefficient of the imine, which is much larger than that of isobutyraldehyde at its absorption maximum. It will also permit the use of lower concentrations of isobutyraldehyde so that complications due to isobutyric acid in the aldehyde solution will be less.

Because the absorption of amine at the absorption maximum of imine is significant, the same concentration of amine solution as the initial concentration of amine in the sample cell was used in reference cell in the runs in which measurements were made at the imine absorption maximum. In this case, Equation (14) and (15) will change to the form:

$$\frac{A_o}{A_oE_A + E_B(B_o - B') - D} = \frac{1}{E_A + E_B - E_I} + \frac{1}{KB(E_A + E_B - E_I)} \qquad (16)$$

$$\frac{A_o}{D - A_oE_A - E_B(B_o - B')} = \frac{1}{E_I - E_A - E_B} + \frac{1}{KB(E_I - E_A - E_B)} \qquad (17)$$

where B′ is the concentration of amine in the reference cell. Similarly, Equation (14′) and (15′) have the corresponding form.

$$\frac{A_o}{A_oE_A + E_B(B_o - B') - D} = \frac{1}{E_I - E_B - E_A} + \frac{W}{K'B(E_A + E_B - E_I)} \qquad (16')$$

$$\frac{A_o}{D - A_oE_A - E_B(B_o - B')} = \frac{1}{E_I - E_B - E_A} + \frac{W}{K'B(E_I - E_A - E_B)} \quad (17')$$

In order to use Equations (14) through (17'), it is necessary to know the values of B and B_o in the various equilibration solutions. The total concentration of amine in all forms, B_T, may be calculated from the volumes of the various solutions and the strengths of the amine solutions used in making up the equilibrium solutions. Inasmuch as B_T is equal to B_o plus BH^+, and BH^+, the ammonium ion concentration is always quite small, B_o is set equal to B_T as a first approximation. In some cases, where K is rather small and B_T reasonably large, B is also set equal to B_T as a first approximation. Otherwise, if measurements are being made at the imine maximum, the first approximation of the value of B is made by attributing all the absorption to imine, thus estimating I, and subtracting the estimated I from the first approximation of the B_o value.

The value of A_o, the total concentration of aldehyde in all forms, may be calculated from the manner in which the equilibrium solutions were made up. If an estimate of the concentration of imine, I, has been made, a first approximation to the value of K may be made by substituting into Equation (8) as follows.

$$K = \frac{I}{AB} = \frac{I}{(A_o - I)(B_o - I)}$$

If the value of I has not been estimated, then Equation (14) (or a more suitable equation from the series (15) through (17')) may be used to obtain a first approximation of K. Values of $A_o/(A_oE_A + B_oE_B - D)$

are plotted against 1/B. The value of E_B and D are measured and the A_oE_A value comes from simultaneous measurements on solutions like the equilibrium solutions except that the amine has been omitted. The first approximation to the values of B and B_o are used. The intercept in the plot is equal to $1/(E_A + E_B - E_I)$ and the slope is $1/K(E_A + E_B - E_I)$; therefore, K is calculated by dividing the intercept by the slope.

In an improved calculation of K, it is necessary to make correction for the amount of the amine that is tied up as the ammonium ion. The ammonium ions present arise partly from isobutyric acid, which we have been unable to remove entirely from the isobutyraldehyde in the purification procedures employed, in spite of the fact that the aldehyde is distilled, stored, and handled under nitrogen. At the pH's prevailing in our equilibrium solutions isobutyric acid will exist essentially completely in the form of isobutyrate anions. From B_T, the total concentration of amine in all forms, p, the concentration of isobutyrate (determined by titration of the aldehyde solutions used), and K_b, the ionization constant of the amine at 35^o and the appropriate ionic strength, we can calculate the concentration of ammonium ion

$$BH^+ = \frac{p - K_B + \sqrt{(-p + K_b)^2 + 4K_b(B_T - I)}}{2} \qquad (18)$$

Subtraction of the ammonium ion concentration from B_T gives a new value for B_o. Then using this new B_o and the experimentally determined value of E_B, new values of B_oE_B and/or $E_B(B_o - B')$ are calculated.

Improved values of B for the various points may be calculated from the latest B_o and K as shown below:

$$I = B_o - B = \frac{KAB}{1 + KB} \tag{19}$$

where K is the equilibrium constant determined in the first approximation (or from pH measurements if available).

From Equation (19), solving for B, we get

$$B = \frac{B_o - A_o - \frac{1}{K} + \sqrt{(B_o - A_o - \frac{1}{K})^2 + \frac{4B_o}{K}}}{2} \tag{20}$$

or if W and K′ are used

$$B = \frac{B_o - A_o - \frac{W}{K} + \sqrt{(B_o - A_o - \frac{W}{K})^2 + \frac{4B_oW}{K}}}{2} \tag{21}$$

is obtained.

By using Equation (20) or Equation (21) the concentration of amine left in the solution is obtained.

Then, if Equation (17) is used,

$$\frac{A_o}{D - A_oE_A - E_B(B_o - B')}$$

is plotted against $\frac{1}{B}$ (or, if Equation (17′) is used, $\frac{W}{B}$). Through the experimental points the best straight line is drawn.

If the K (or K′) value determined from this line is not equal to that obtained in the previous approximation, it is considered to be an improved approximation and used as the basis for going through the procedure of calculation again. The process of successive approximations is continued until the value obtained no longer changer. It is necessary to go through the process three times in most cases and never more than four times. The calculation was done by a Burroughs B-5000 computer (see Appendix).

The extinction coefficients of the imines are about ten times as large as the apparent extinction coefficient of the aldehyde. This permits considerably more dilute solutions to be used when K is determined by measurements at the imine maxima, so that complications due to the isobutyric acid present as an impurity in the aldehyde are minimized. It is also much less likely that the concentration of imine will become so large as to cause imine to separate from solution.

CHAPTER III

IONIZATION CONSTANTS

Autoprotolysis Constant of Water

The interrelationship between the concentrations of hydrogen and hydroxyl ions in an aqueous medium is fixed by the equilibrium between these ions and water molecules:

$$H_2O \rightleftarrows H^+ + OH^- \tag{22}$$

Since the purest water is dissociated into H^+ and OH^- to an extremely slight degree, Equation (22) must be written as a reversible reaction. Applying the mass law to this reaction in equilibrium, we may write:

$$K_W = m_H m_{OH} \tag{23}$$

or

$$K'_W = [H^+][OH^-] \tag{24}$$

in terms of molal concentrations (m's) or molar concentrations (in brackets). Although such equilibrium constants will vary with ionic strength, this is not true of a thermodynamic equilibrium constant such as

$$K_W^t = \frac{m_H m_{OH} \gamma_H \gamma_{OH}}{a_{H_2O}} \tag{25}$$

where a_{H_2O} is the activity of water and the γ's are activity coefficients.

The process represented by Equation (22) has a large heat effect; accordingly, the temperature coefficient of K_W is large. The activity coefficients in Equation (25) are practically unity unless solutes are present. If aH_2O is defined as unity in water, K_W is equal to K_W^t at zero ionic strength.

Values of K_W^t at temperatures from 0° to 60° C at 5° intervals are listed in Table 32 (Appendix).

In this study the equilibrium constants for imine formation are determined at 35° and various ionic strengths (other than zero). The dissociation constant of water at 35° and various ionic strength is required for this investigation.

Harned and Hamer (42) used the cell

$$H_2|HX(m_1),\ MX(m_2)|AgX\text{-}Ag$$

to determine the dissociation constant of water. The electromotive force of such a cell at a given temperature is given by

$$E = E_o - \frac{RT}{F} \ln \gamma_H \gamma_X m_H m_X \qquad (26)$$

where E_o is the electromotive force of the standard cell, which is equal to 0.21563 volt at 35° (43).

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42. H. S. Harned and W. J. Hamer, J. Am. Chem. Soc., 55, 2194 (1933).

43. H. S. Harned and R. W. Ehlers, J. Am. Chem. Soc., 54, 1350 (1932).

Elimination of m_H from Equations (25) and (26), and rearrangement of resulting terms gives

$$E - E_o + \frac{RT}{F} \ln \frac{m_X}{m_{OH}} = \frac{RT}{F} \ln \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} - \frac{RT}{F} \ln K_W^t - \frac{RT}{F} \ln \gamma_H \gamma_X \quad (27)$$

The values of the ionic activity coefficient product of water,

$$\frac{\gamma_H \gamma_{OH}}{a_{H_2O}},$$

for the particular ionic strengths and salts used by Harned and co-workers were obtained by Equation (27). The values in potassium chloride, sodium chloride, and sodium bromide at 35^o are listed in Table 1.

The dissociation constant of water in terms of molarity can easily be obtained by substitution of the ionic activity function in Table 1 into Equation (25). The values obtained are listed in the columns headed K_W, Table 2.

Harned and co-workers have given equations for the relationship between molarity and molality in the presence of various concentrations of potassium chloride (46), sodium chloride (47), and sodium bromide (48).

By applying these equations, values for the dissociation constants of water, K_W, in terms of molarity were calculated and are shown in the columns headed K'_W, in Table 2.

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46. H. S. Harned and M. A. Cook, J. Am. Chem. Soc., 59, 1290 (1937).

47. H. S. Harned and M. A. Cook, J. Am. Chem. Soc., 61, 495 (1939).

48. H. S. Harned and C. C. Crowford, J. Am. Chem. Soc., 59, 1903 (1937).

Table 1. The Ionic Activity Function of Water, $\frac{\gamma_H \gamma_{OH}}{a_{H_2O}}$ in Salt Solutions at 35°.

	Ionic Activity Function of Water		
μ	KCl (42)	NaCl (44)	NaBr (45)
0.01	0.812	-	-
0.02	0.754	0.756	0.765
0.03	0.720	0.720	0.726
0.04	0.696	-	0.699
0.06	0.662	0.658	0.660
0.11	0.612	0.600	0.606
0.21	0.567	0.549	0.561

44. H. S. Harned and G. E. Mannweiler, J. Am. Chem. Soc., 57, 1873 (1935).

45. H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions, 3rd. ed., Reinhold Publishing Corporation, New York, 1958, p. 752.

Table 2. Dissociation Constant of Water in Terms of Molality (K_W) and Molarity (K'_W) at 35°.

μ'[a]	μ[b]	KCl		NaCl		NaBr	
		K_W	K'_W	K_W	K'_W	K_W	K'_W
0	0	2.088	2.062	2.091	2.065	2.089	2.064
0.0100	0.0099	2.573	2.540	-	-	-	-
0.0200	0.0199	2.771	2.734	2.763	2.728	2.731	2.695
0.0300	0.0298	2.901	2.862	2.901	2.863	2.877	2.838
0.0400	0.0397	3.001	2.959	-	-	2.989	2.947
0.0600	0.0596	3.156	3.108	3.175	3.130	3.165	3.118
0.1100	0.1091	3.413	3.352	3.482	3.426	3.447	3.387
0.2100	0.2077	3.684	3.599	3.805	3.730	3.724	3.639

[a] In terms of molality.

[b] In terms of molarity.

[c] Extrapolated value.

Table 3. pK'_W of Water at 35° C.

m	C	pK'_W		
		KCl	NaCl	NaBr
0	0	13.686	13.685	13.685
0.0100	0.0099	13.595	-	-
0.0200	0.0199	13.563	13.564	13.569
0.0300	0.0298	13.543	13.543	13.547
0.0400	0.0397	13.529	-	13.531
0.0600	0.0596	13.507	13.505	13.506
0.1100	0.1091	13.475	13.465	13.460
0.2100	0.2077	13.444	13.428	13.439

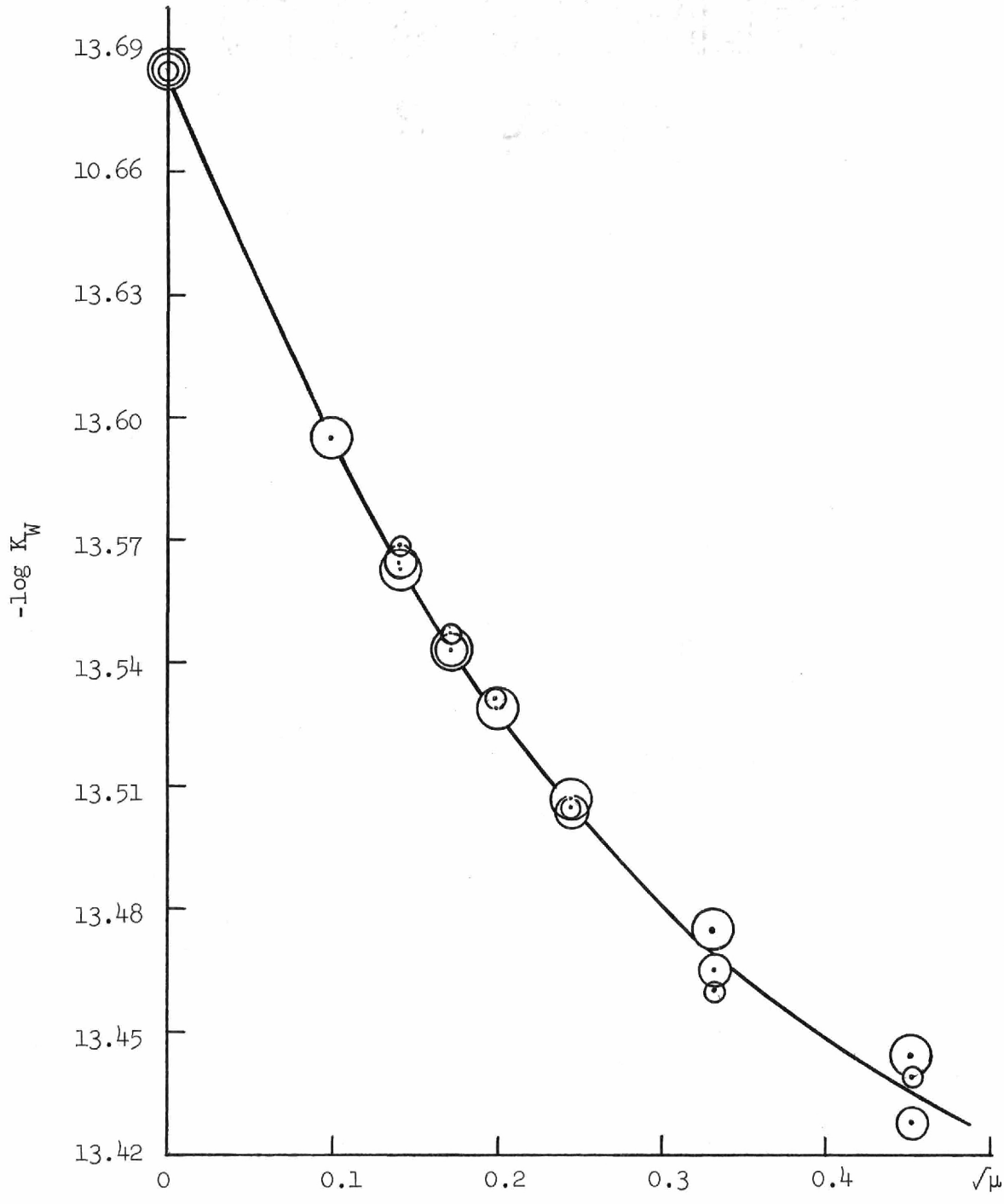

Figure 1. Dissociation Constant of Water at 35° C.

It may be seen that the value of K_W in dilute solution is essentially independent of the nature of the salt present at a given ionic strength.

The difference between the values of pK'_W in the presence of different salts at a given ionic strength increases as the ionic strength of the solution is increased. For convenience, the values of pK'_W were plotted against the square root of ionic strength (in terms of molarity). As shown in Figure 1, only one curve was plotted through the three sets of experimental points. One can easily read the average value of pK'_W at any desired ionic strength. Since pK′ has about the same value at ionic strength below 0.06 M in the presence of the three different salts, sodium chloride, sodium bromide, and potassium chloride, at a given ionic strength, it will be assumed to have the same value at the same ionic strength in our equilibrium solutions where the ionic strength is never above 0.02 M.

Ionization Constant of Methylamine

In 1941, Everett and Wynne-Jones (49) determined the ionization constant of methylamine in water from 0° to 50° at 10° intervals and ionic strengths from 0.05 to 0.20, and extrapolated these data to zero ionic strength. They used the cell

$$H_2 \left| \begin{matrix} HCl \\ KCl \end{matrix} \right| KCl\ 3.5M \left| \begin{matrix} MeNH_2 \\ MeNH_2.HCl \\ KCl \end{matrix} \right| H_2$$

and measured the e.m.f. The following results were obtained. (Table 4).

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49. D. H. Everett and W. F. K. Wynne-Jones, Proc. Roy. Soc., (London), A 177, 499 (1941).

Table 4. pK_a of Methylammonium Ions

Conc. M	-log K_o	-log K_{10}	-log K_{20}	-log K_{30}	-log K_{40}	-log K_{50}
0.1988	11.5845	11.2170	10.8705	10.5440	10.2360	9.9450
0.1491	11.5685	11.2005	10.8520	10.5265	10.2200	9.9320
0.0994	11.5460	11.1790	10.8330	10.5080	10.2015	9.9145
0.0497	11.5225	11.1550	10.8100	10.4875	10.1820	9.8950
0[a]	11.4960	11.1300	10.7870	10.4660	10.1605	9.8760

[a]Extrapolated Value.

In Table 4, if -log K_a values at zero ionic strength are plotted against $\frac{1}{T}$, -log K_a at zero ionic strength and 35° can be obtained. Similarly, plots of -log K_a against $\frac{1}{T}$ gave -log K_a at 35° and ionic strength 0.0497, 0.0994, 0.1491, and 0.1988 (in terms of molarity), respectively. Finally, from the K_W and K_a values at various ionic strengths and 35°, the corresponding K_b values are obtained. If K_b values are plotted against the square root of ionic strength, a straight line can be drawn, from which one can read the ionization constants at various ionic strengths directly. For convenience, the plot at low ionic strength has been enlarged as shown in Figure 2; some of the values obtained from this plot are listed in Table 5.

Ionization Constant of n-Propylamine

The free energy for the equilibrium between n-propylamine and n-propylammonium ion in water was measured by Evans and Hamann (50), using the same type of cell that Everett and Wynne-Jones used in determining the ionization constant of methylamine. The values at ionic strengths 0.0497, 0.0994, 0.1988 (in terms of molarity), and temperature 20° C and 40° C were reported (Table 6). The value at zero ionic strength has also been estimated by extrapolation.

From the standard molar free energy change for the reaction

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}NH_2 + H_2O \rightleftarrows CH_3\text{-}CH_2\text{-}CH_2\text{-}NH_3^+ + OH^-$$

and applying the equation

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50. A. G. Evans and S. D. Hamann, Trans. Faraday Soc., 47, 34 (1951).

Table 5. Ionization Constant of Methylamine at 35°.

μ	$-\log K_a$	$-\log K_b$	$K_b \times 10^4$
0	10.310	3.375	4.22[a]
0.0099	10.314	3.281	5.24
0.0199	10.316	3.250	5.62
0.0298	10.320	3.225	5.96
0.0397	10.324	3.206	6.22
0.0596	10.330	3.176	6.67

[a]From extrapolation to infinite dilution

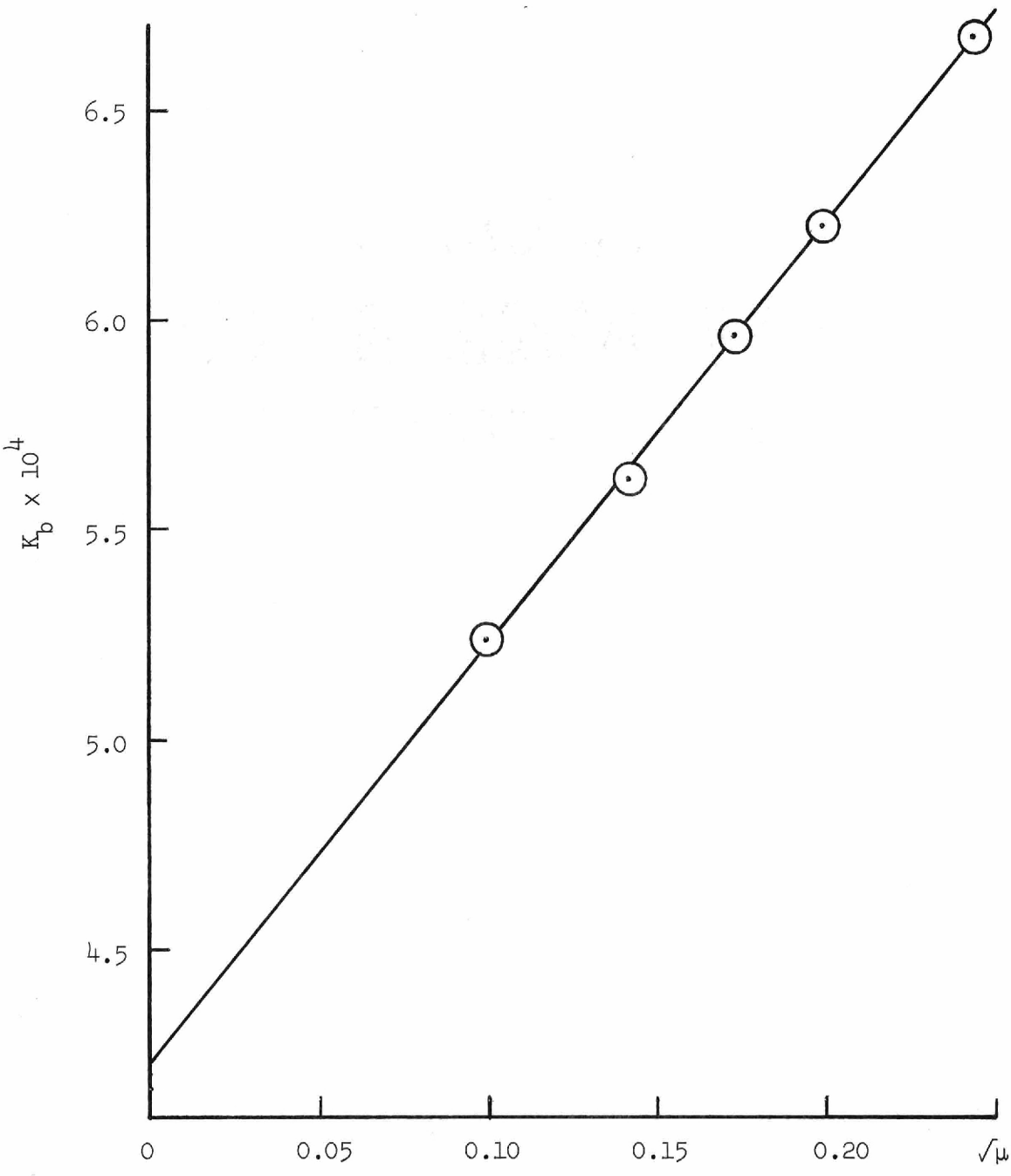

Figure 2. Ionization Constant of Methylamine at 35° C

Table 6. Free Energy for the Equilibrium of n-Propylamine and its Ammonium Ion in Water.

μ.m.	T, °C	-ΔG cal/mol.
0.1988	20	14414
0.1988	40	14446
0.0994	20	14382
0.0994	40	14412
0.0497	20	14373
0.0497	40	14409
0[a]	20	14357
0[a]	40	14391

[a]Extrapolated value.

$$\Delta G = -RT \ln K \qquad (28)$$

the ionization constants at those particular ionic strengths and temperatures were calculated.

The ionization constants are plotted against reciprocal of temperature, $\frac{1}{T}$, for the ionic strengths 0, 0.0497, 0.0994, and 0.1988 M respectively. From these plots the values at these ionic strengths and 35° can be obtained. The ionization constants at 35° are then plotted against the square root of ionic strength. For convenience, an enlarged part of the plot is shown in Figure 3, and some of the values obtained from it are shown in Table 7.

Ionization Constant of 3-Methoxypropylamine

The dissociation constant of 3-methoxypropylamine has not been reported in the literature. It has been determined by titrating 3-methoxypropylamine with perchloric acid at various ionic strengths at 35°. A research pH meter (sensitive to 0.001 pH) is used in this determination. Considering the following equation

$$RNH_3^+ \rightleftarrows RNH_2 + H^+ \qquad (R = CH_2\text{-}CH_2\text{-}CH_2\text{-}OCH_3)$$

the dissociation constant can be written as

$$K_a = \frac{[RNH_2][H^+]}{[RNH_3^+]}$$

Because the concentration of hydrogen ion is small during the titration, at the half way point of neutralization, the pK_a value is equal to the pH value.

Table 7. Ionization Constants of n-Propylamine at 35°.

μ,M	-log K_a	-log K_b	$K_b \times 10^4$
0[a]	10.212	3.473	3.37
0.0099	10.217	3.378	4.19
0.0199	10.219	3.347	4.50
0.0298	10.221	3.324	4.75
0.0397	10.223	3.307	4.93
0.0596	10.226	3.280	5.25

[a]Extrapolated Value.

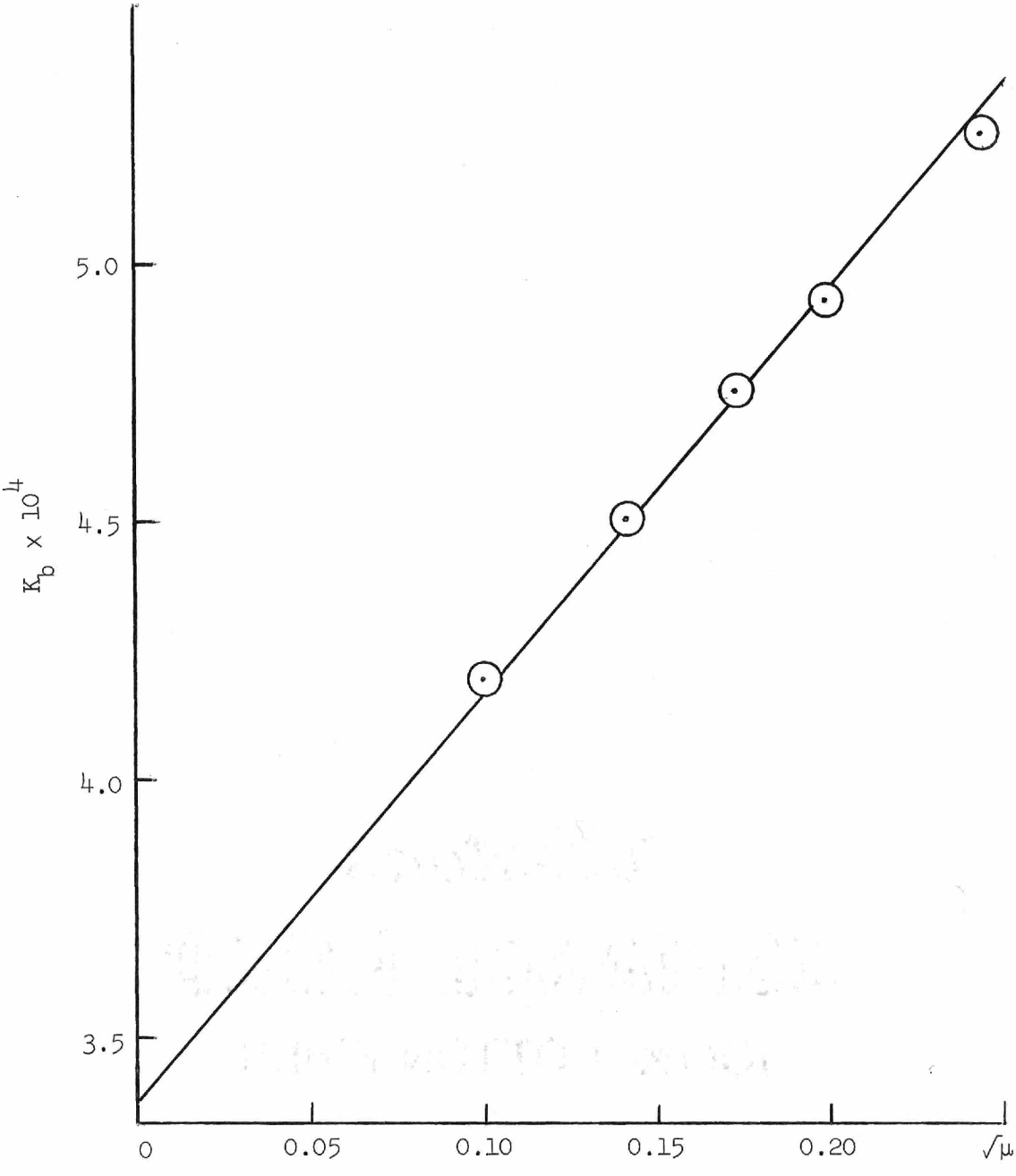

Figure 3. Ionization Constant of n-Propylamine at 35° C.

It is not always easy to find the end point accurately by inspection of the curve in which the pH values are plotted against volume, but it can be found much more accurately by a differential plot, in which the difference in pH values per unit volume of perchloric acid, $\Delta pH/\Delta V$, is merely the slope of the curve (pH against volume) at any value of volume; the differential plot is therefore a means of locating more accurately the volume of titrant at the maximum slope of the ordinary titration curve.

The dissociation constants at four different ionic strengths have been obtained directly by titration. The value at zero ionic strength is obtained by extrapolating the curve, in which the dissociation constants are plotted against the square root of ionic strength, to zero ionic strength (Figure 4). All of these values are shown in Table 8.

Ionization Constant of t-Butylamine

The dissociation of t-butylammonium ion may be formulated as

$$\text{t-BuNH}_3^+ + H_2O \rightleftarrows \text{t-BuNH}_2 + H_3O^+$$

The dissociation constant was determined by Hetzer, Robinson, and Bates (51) using a cell which may be represented as

$$Pt - H_2(g{:}1atm)\,|\,(CH_3)_3CNH_3Br(m_1),(CH_3)_3CNH_2(m_2)\,|\,AgBr\text{-}Ag$$

where m's are molality. The results of their measurements of the electromotive force of the above cell at 35° are listed in Table 9.

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51. H. B. Hetzer, R. A. Robinson, and R. G. Bates, J. Phys. Chem., 66, 2696 (1962).

Table 8. Ionization Constant of 3-Methoxypropylamine at 35°.

μ	pK_a	pK_b	$K_b \times 10^4$
0	9.718	3.967	1.08[a]
0.00435	9.845	3.778	1.67
0.00771	9.849	3.756	1.75
0.05135	9.946	3.569	2.70
0.09853	9.950	3.525	2.99

[a]From extrapolation to infinite dilution.

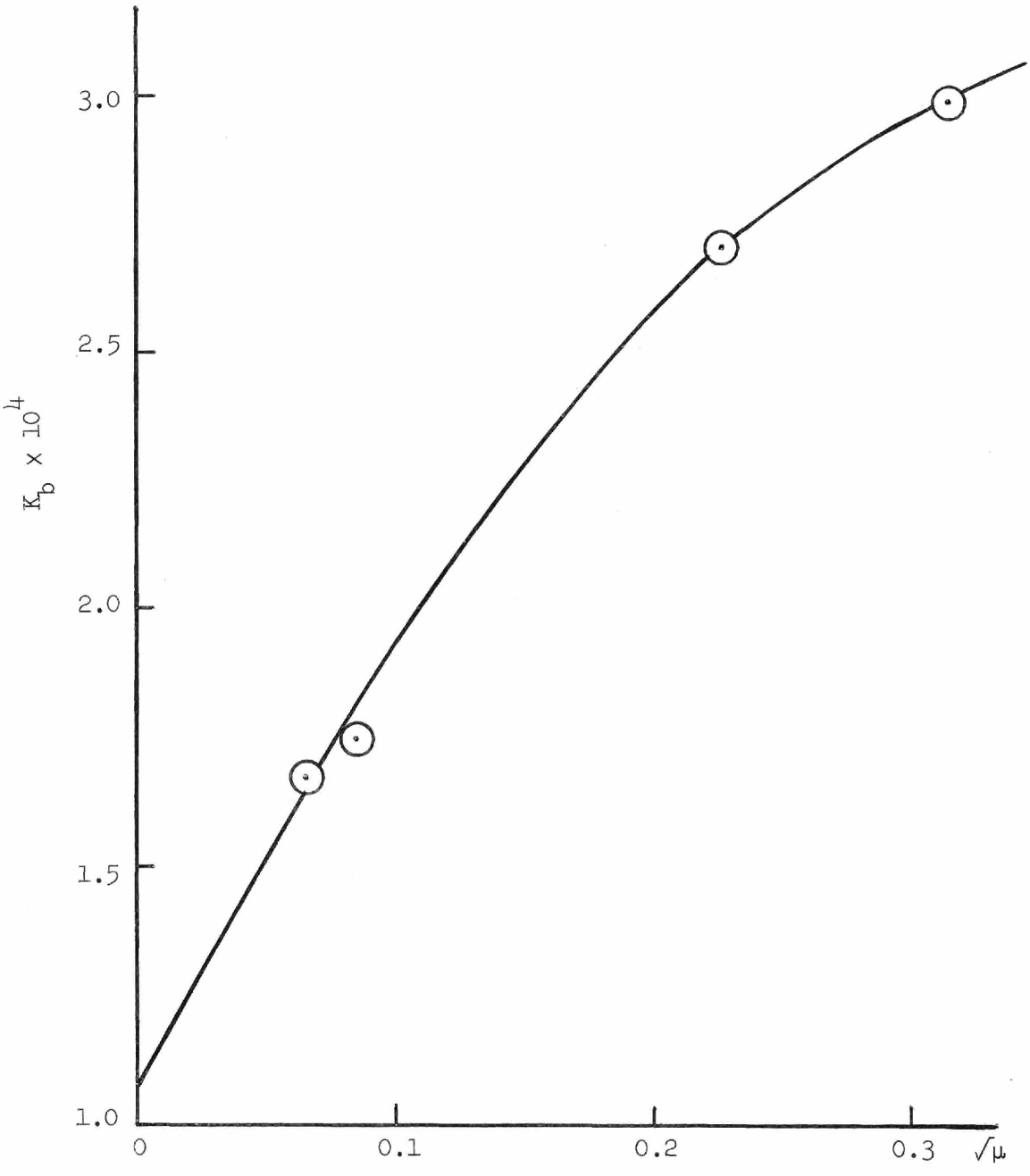

Figure 4. Ionization Constant of 3-methoxypropylamine at 35° C.

The general equation for calculating the acidic dissociation constant, K_a, is obtained by combining the mass-law expression for the above reaction with the Nernst equation for the cell and with the DeBye-Hückel expression for the activity coefficient of the ions concerned (52). The resulting equation is

$$-\log K_a' = -\log K_a - \beta\mu$$

$$= -\log (\gamma_H \gamma_H m_H) + \log \frac{m_{BH}^{+}}{m_B} - \frac{2a\sqrt{\mu}}{1 + b\alpha\sqrt{\mu}} \qquad (29)$$

where

$$-\log (\gamma_H \gamma_X m_H) \equiv \frac{E - E_o}{2.30259 \frac{RT}{F}} + \log m_X \qquad (30)$$

In these equations, E and E_o and the e.m.f. and standard potential of the cell, a and b are Debye-Hückel constants,[1] μ is the ionic strength, α and β are adjustable parameters.

It is evident that in Equation (29) K_a' is a concentration dissociation constant which becomes equal to the thermodynamic dissociation constant K_a, at zero ionic strength.

By applying Equation (29), where E_o = 0.06585 (53), R = 8.3143 joules/deg. moles, F = 96, 487.0 coulombs/equiv., T = 308.150, α = 0 and a = 0.5211,[2] B = 0.3312,[2] the values of dissociation constants were

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52. H. B. Hetzer and R. G. Bates, J. Phys. Chem. 66, 308 (1962).

53. H. B. Hetzer, R. A. Robinson, and R. A. Bates, J. Phys. Chem., 66, 1423 (1962).

[1] Cf. appendix Table 32.

[2] Cf. appendix Table 33-34.

Table 9. Ionization Constant of t-Butylamine at 35° C.

$(CH_3)_3CNH_3Br$	$(CH_3)_3CNH_2$	E volt(46)	$K_b \times 10^4$
0.04724	0.02359	0.77171	5.90
0.04256	0.02126	0.77396	5.85
0.04045	0.01983	0.77462	5.85
0.03592	0.01818	0.77784	5.77
0.03374	0.01655	0.77837	5.73
0.02421	0.01225	0.78654	5.57
0.01293	0.00634	0.79925	5.16
			4.53[a]

[a]Value extrapolated to zero ionic strength by Hetzer, Robinson and Bates (51).

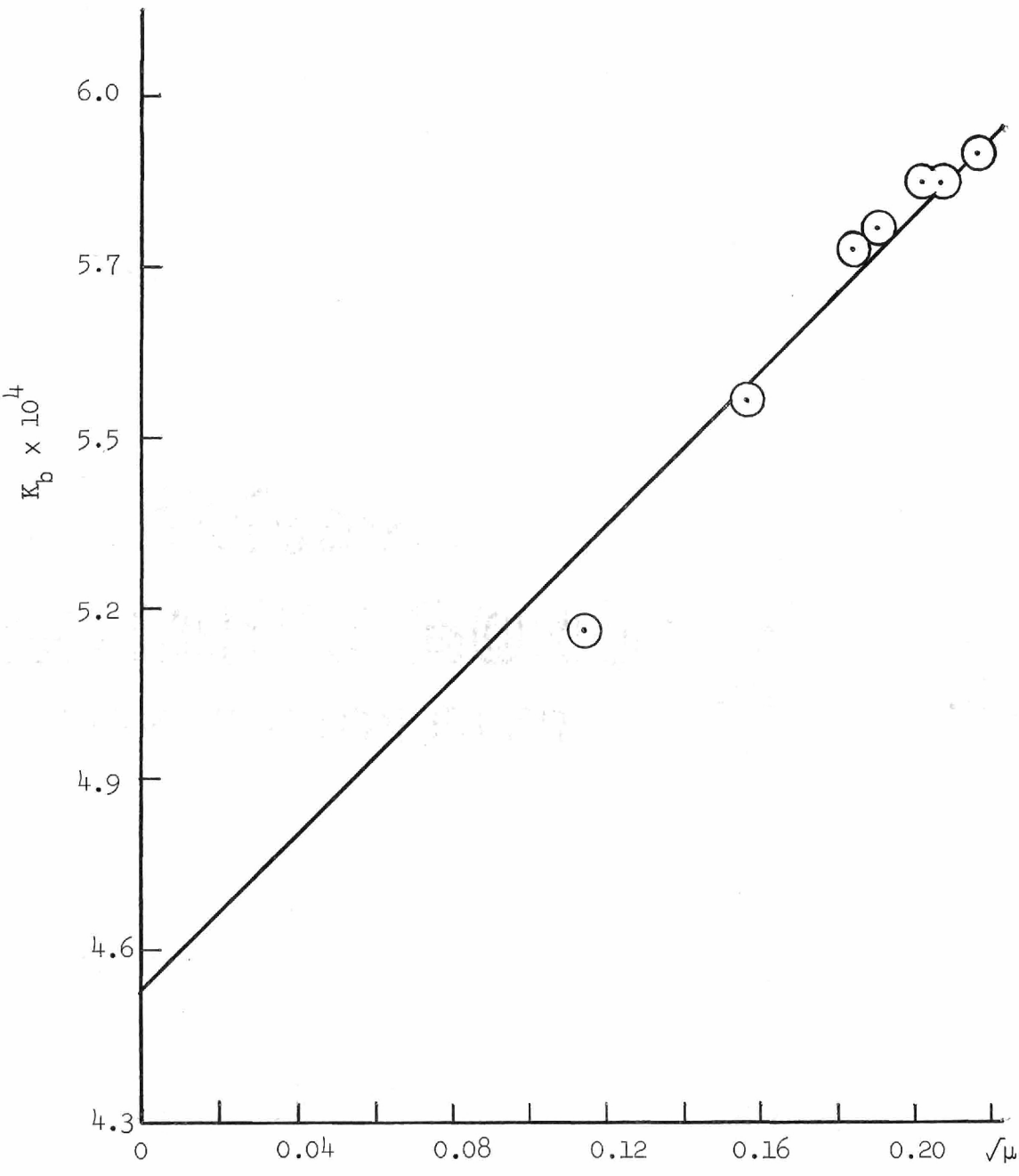

Figure 5. Ionization Constant of t-Butylamine at 35° C.

calculated in terms of molarity and shown at the right column of Table 9. A plot of dissociation constant against the square root of ionic strengths (in terms of molarity) is shown in Figure 5.

CHAPTER IV

EXPERIMENTAL AND INSTRUMENTATION

Chemicals[3]

t-Butylamine

Eastman white label t-butylamine was distilled under nitrogen.

Bromothymol blue

Fisher Scientific Company bromothymol blue was used. One-tenth gram of bromothymol blue was dissolved in 100 ml of 20% aqueous ethanol.

Isobutyraldehyde

Eastman Chemical Company isobutyraldehyde was distilled under nitrogen.

Methylamine

Matheson Coleman and Bell Company 25% aqueous methylamine was used.

3-Methoxypropylamine

Eastman Chemical Company practical grade 3-methoxypropylamine was distilled under nitrogen.

Perchloric Acid

Baker Analyzed Reagent grade perchloric acid was used without further purification.

Potassium Hydroxide

Baker Analyzed Reagent grade solid potassium hydroxide was used.

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[3]The boiling points that were determined are listed in Table 10 at the end of this section.

n-Propylamine

Eastman Organic Chemical Company practical grade propylamine was distilled under nitrogen.

Sodium Hydroxide

Baker Analyzer Reagent grade sodium hydroxide was used.

Standard Buffer Solutions

Beckman 14049 buffer (pH = 9.18 at 25° C) and Beckman 3501 Buffer (pH = 7.00 at 25° C) were used.

Instrumentation

Ultraviolet Measurements

All the ultraviolet spectra were made with a Cary Recording Spectrophotometer, Model 14. The instrument was operated as described in the operating manual. The spectra were made using distilled water as the solvent unless otherwise indicated. A matched set of Beckman No. 46007 quartz one-centimeter cells was used for all measurements. Distilled water was used in the reference cell in obtaining extinction coefficients, except in certain cases, which will be noted, where a variety of aqueous amine solutions were used. Water at 35° was circulated around the cell compartment and cell holder from a constant temperature bath. Since 35° is higher than room temperature, the solution required a few minutes to attain thermal equilibrium. For each imine, the wavelength of maximum absorption was first determined. Then, the instrument was fixed at this particular wavelength to obtain the optical density. This has the advantage of making sure that the solution is at thermal equilibrium.

Table 10. Boiling Points of Some Chemicals Used.

Compound	Observed Value[a]	Literature Value
Isobutyraldehyde	63.5 ~ 64°	63.5° (54)
Propylamine	47°	48.0° (55)
3-Methoxypropylamine	115 ~ 116°	117-118° (56)
t-Butylamine	44-45°	44.5° (57)

[a]Under atmospheric pressure (740-745 mm Hg).

54. D. I. Coomber and J. R. Partington, J. Chem. Soc., 1444 (1938).

55. A. I. Vogel, J. Chem. Soc., 1829 (1948).

56. W. P. Utermohlen, Jr., J. Am. Chem. Soc., 67, 1505 (1945).

57. M. T. Rogers, J. Am. Chem. Soc., 69, 457 (1947).

pH Measurements

A Beckman 101900 Research pH Meter with glass electrode and calomel reference electrode was used in this experiment. In the measurement of pH with this particular pH meter, the instrument is calibrated first against an internally contained standard cell at 1019.44 millivolts; this potential is known precisely at any given ambient temperature. Then, for the purpose of standardizing the electrode system, the electrode tips are immersed in a buffer solution of known pH. In this standardization procedure, the temperature compensator is set to the temperature of the buffer (at 35° C), while the read control is set to the exact pH value of the buffer at its measured temperature. The standardize control is adjusted until the null meter is balanced, thus compensating for the various potentials in the electrode system. Subsequent immersion of the electrode tips in a sample solution causes a potential that is proportional to the pH of the sample. This potential is balanced out by adjusting the read control until the null meter is balanced. The potential is read directly in pH units on the readout scales. The sensitivity is ± 0.001 pH.

The pH scale was standardized at a pH of 6.99 by Beckman buffer 3501 or at pH of 9.10 by Beckman buffer 14049 at 35°. The measurements were made on equilibration solutions stirred with a magnetic stirrer in a beaker which was in a water bath at 35°.

Constant Temperature Baths

A constant temperature water bath made by Precision Scientific Company No. 587, was used for all extended studies at 35°. This was connected to a Sargent Laboratory Thermoregulator, No. 3829, and water

was circulated around the cell compartment and cell holder during ultraviolet measurements, while in pH measurements, the water was circulated through copper tubing in a small basin which held the beaker for titration. The bath temperature was adjusted to 35.0 $\pm$ 0.2° using a -2 to 68° C thermometer with 0.2° divisions in the thermostat. The temperature of the equilibrium solution was checked periodically by using a special thermometer (-1 to 40° with 0.2° divisions).

Nuclear Magnetic Resonance Measurements

The nuclear magnetic resonance (n.m.r.) spectra were obtained from a Varian Nuclear Magnetic Resonance Spectrometer, Model A-60. In order to obtain a reasonable signal, the r.f. frequency was set at 0.04 to 0.10 units, the filter bandwidth at 0.4 to 4 c.p.s. and the sweep time was 250 sec. The instrument was zeroed with internal tetramethylsilane in neat samples. All chemical shifts (δ) are given in cycles per seconds (c.p.s.) downfield from the internal reference. For all spectra given as figures 500 cps and 50 cps sweep widths were used.

Boiling Point Determination

Boiling points were taken as the distillation temperature of the fraction collected. All boiling points reported herein are uncorrected.

Infrared Measurements

All infrared (IR) spectra were recorded with a Perkin-Elmer Infrared Spectrophotometer, Model 21, and calibrated with the 6.238 μ band of polystyrene.

Refractive Index Measurements

All refractive indices were measured using a Bausch and Lomb

Abbé-56 refractometer.

Preparation of N-Isobutylidenealkylamines

The N-isobutylidenealkylamines were prepared by a method based on that of Campbell, Sommers and Campbell (36). For the case of the methylimine this method is described in detail as follows. The aqueous methylamine (~ 25%) obtained from the Matheson Coleman and Bell Company was used without further purification. Fifty-eight milliliters of 25% aqueous methylamine (or 16 g. of methylamine) was added to a 300 ml. three-necked round bottom flask which was cooled in an ice-salt bath. One of the necks was connected with a condenser, the central neck connected with a dropping funnel which contained 50 ml. (or 37 g.) freshly distilled isobutyraldehyde, and the third neck was connected with a T tube leading to a prepurified nitrogen cylinder.

The aldehyde was added slowly to the amine with magnetic stirring and the system was kept in the ice-salt bath to guard against excess heat of reaction. The stirring was continued for one hour. Then, the solid potassium hydroxide was added and stirring was continued for over fifteen minutes.

The flask was then allowed to warm to room temperature. The water layer was separated by using a separatory funnel, then the product was dried overnight with solid potassium hydroxide in the refrigerator. Finally, it was distilled under nitrogen, b.p. 69.5°, 35.2 g (81% yield).

N-Isobutylidene-n-propylamine, N-isobutylidene-3-methoxypropylamine, and N-isobutylidene-t-butylamine were prepared by the same

Table 11. Yields of N-Isobutylidenealkylamines

Compound	Aldehyde Used g.	Amine Used g.	Yield %
N-Isobutylidenemethylamine	37	16	81
N-Isobutylidene-n-propylamine	39	32	77
N-Isobutylidene-3-methoxypropyl-amine	24	30	90
N-Isobutylidene-t-butylamine	36	38	59

Table 12. Physical Constants of Some N-Isobutylidenealkylamines

$(CH_3)_2CH-CH=N-R$ R	B.P	d_4^t	n_D^t	t
Methyl	69.5	0.7388[a]	1.4041[a]	12.5
n-Propyl	115.5	0.7518[a]	1.4158[a]	13.5
3-Methoxypropyl	160.0	0.8202	1.4245	b
t-Butyl	115-116	0.7453	1.4055	25.0

[a] R. T. Tiollais, Bull. Soc. Chim. France, 14, 708 (1947).

[b] For density at 35°, for refractive index at 25°.

apparatus and procedures. The amounts of materials used and yields obtained are listed in Table 11. Physical constants of these imines are listed in Table 12.

N-Isobutylidene-3-methoxypropylamine has not been reported in the literature. The elemental analysis of this compound give

	%C	%H	%N
Found	67.09	11.82	9.93
Calculated	67.07	11.97	9.79

pH Measurements

N-Isobutylidenemethylamine

Methylamine-Methylammonium Buffer Solution. A 250 ml. volumetric flask was filled 95% with nitrogen-saturated water, 1.0 ml. of 25% aqueous methylamine was added, and then water was added to the mark. Two 20-ml. aliquots were titrated with standard acid to determine the amine concentration. To 200 ml. of this methylamine solution was added 3.90 ml of 0.51578 M hydrochloric acid. The concentration of methylammonium ion, 0.0108 M and concentration of methyamine (in Table 13) were calculated.

Isobutyraldehyde Solution. A 0.2 M solution of isobutyraldehyde was made up in nitrogen-saturated water in a 250 ml. volumetric flask. In order to make sure the nitrogen-aldehyde solution was neutral when added to the amine solution, 0.75 ml. of bromothymol blue solution was added and the solution was neutralized by standard sodium hydroxide solution. The change in aldehyde concentration due to oxidation to acid and to change in volume by adding indicator and base has been accounted

for. The addition of aldehyde solution was carried out under nitrogen to prevent the oxidation of isobutyraldehyde. The temperature was kept at 35 ± 0.2°. A research pH meter was used to make the following measurements.

In each experiment the aqueous isobutyraldehyde solution was added to 100 ml. of methylamine-methylammonium buffer solution. The brackets in Table 13 represent the concentration of solution before the addition of isobutyraldehyde.

Applying Equations (4-8) and the ionization constants of methylamine and water in Chapter III, the equilibrium constant is calculated as shown in the righthand columns of Table 13. The average concentration of water in these experiments, 54.87 M., is calculated from the partial molar volumes of aldehyde and amine and their concentrations.

N-Isobutylidene-n-propylamine

n-Propylamine-n-propylammonium Buffer Solution. An aqueous n-propylamine solution with a concentration of 0.21 M was prepared from freshly distilled n-propylamine and nitrogen-saturated distilled water in a 250 ml. volumetric flask. Then, 4.00 ml. of 0.51587 M of hydrochloric acid was added to this amine solution. The concentration of n-propylammonium ion, 91.2×10^{-4} M; and n-propylamine (given in Table 14) were calculated.

Isobutyraldehyde Solution. The aldehyde solution was prepared in a concentration approximately equal to that of the n-propylamine. The procedure and amounts of indicator added are exactly the same as described before. Isobutyraldehyde solution was added to 100 ml. of n-propylamine-n-propylammonium buffer solution at 35° C with magnetic stirring. The data obtained are given in Table 14.

Table 13. Summary of Measuring Equilibrium Constant for N-Isobutylidene-methylamine Formation by pH Measurements.

$[i\text{-PrCHO}]_o$ M	$[i\text{-PrCOOH}]$ 10^4M	$[MeNH_2]_o$ 10^4M	pH of Buffer	Ald. added ml.	pH	K M^{-1}	K′
0.2145	16.5	187.4	10.553	25.0	10.037	85.7	4700
0.2118	15.3	187.6	10.553	25.0	10.039	86.7	4700
0.2104	14.6	191.9	10.564	10.0	10.296	90.2	4950
0.2104	14.6	191.9	10.564	20.0	10.107	85.4	4690
0.2104	14.6	191.9	10.564	30.0	9.967	87.6	4800
0.2104	14.6	191.9	10.564	40.0	9.874	87.3	4780
0.2127	17.2	187.4	10.553	15.0	10.166	91.2	5010
0.2127	17.2	187.4	10.553	20.0	10.076	91.3	5020
0.2127	17.2	187.4	10.553	25.0	10.006	89.4	4910
0.2127	17.2	187.4	10.553	30.0	9.941	90.5	4960
0.2127	17.2	187.4	10.553	35.0	9.886	91.7	5030
0.2127	17.2	187.4	10.553	40.0	9.850	89.6	4910
0.2127	17.2	187.4	10.553	45.0	9.805	91.6	5020
0.2134	17.2	187.4	10.553	15.0	10.178	85.5	4700
0.2134	17.2	187.4	10.553	20.0	10.080	88.7	4870
0.2134	17.2	187.4	10.553	25.0	9.999	91.2	5010
0.2134	17.2	187.4	10.553	30.0	9.935	91.9	5040
0.2134	17.2	187.4	10.553	35.0	9.883	92.2	5060
0.2134	17.2	187.4	10.553	40.0	9.845	90.6	4960
0.2134	17.2	187.4	10.553	45.0	9.805	91.3	5000
				Average		89.5 ± 2.0	4910 ± 90

Table 14. Summary of Measuring Equilibrium Constant for N-Isobutylidene-n-propylamine Formation by pH Measurements.

$[i\text{-PrCHO}]_o$ M	$[i\text{-PrCOOH}]$ 10^4 M	$[n\text{-PrNH}_2]_o$ 10^4 M	pH of Buffer	Ald. Added ml.	pH	K M^{-1}	K′
0.2127	11.6	213.0	10.585	10.0	10.360	71.1	3910
0.2127	11.6	213.0	10.585	15.0	10.260	72.0	3950
0.2127	11.6	213.0	10.585	20.0	10.173	74.5	4090
0.2127	11.6	213.0	10.585	25.0	10.102	75.2	4130
0.2127	11.6	213.0	10.585	30.0	10.039	76.7	4210
0.2127	11.6	213.0	10.585	35.0	9.986	77.8	4260
0.2127	11.6	213.0	10.585	40.0	9.943	76.4	4190
0.2127	11.6	213.0	10.585	45.0	9.901	79.1	4330
0.2153	9.4	214.0	10.587	20.0	10.175	75.4	4140
0.2153	9.4	214.0	10.587	25.0	10.100	75.2	4130
0.2153	9.4	214.0	10.587	30.0	10.046	74.2	4070
0.2153	9.4	214.0	10.587	35.0	9.991	75.8	4160
0.2153	9.4	214.0	10.587	40.0	9.945	76.7	4200
0.2167	8.5	215.0	10.580	20.0	10.163	74.5	4090
0.2167	8.5	215.0	10.580	25.0	10.090	75.6	4150
0.2167	8.5	215.0	10.580	30.0	10.033	75.4	4140
0.2167	8.5	215.0	10.580	35.0	9.980	76.3	4180
0.2167	8.5	215.0	10.580	40.0	9.936	76.7	4200
				Average		75.5 ± 1.3	4140 ± 70

N-Isobutylidene-3-methoxypropylamine

3-Methoxypropylamine-3-Methoxypropylammonium Solution. One milliliter of freshly distilled 3-methoxypropylamine was weighed in a syringe, and then added to a 250 ml. volumetric flask that was almost filled with nitrogen-saturated distilled water. After water was added to the mark, the concentration of amine was about 0.39 M. The buffer solution was prepared by adding 4.0 ml. of 0.51578 M of hydrochloric acid to this amine solution. The concentration of 3-methoxypropylammonium ion is 86.0×10^{-4} M. The concentrations of 3-methoxypropylamine for several runs are listed in Table 15.

Isobutyraldehyde Solution. An isobutyraldehyde solution of the same concentration as that used in determining the equilibrium constant of N-isobutylidenemethylamine was prepared.

In a 250 ml. beaker, 100 ml. of 3-methoxypropylamine-3-methoxypropylammonium buffer solution was titrated with isobutyraldehyde solution. The change in pH values are listed in the following table.

N-Isobutylidene-t-butylamine. The equilibrium constant for the formation of n-isobutylidene-t-butylamine is relatively small. Unfortunately, the change of pH in the titration of t-butylamine-t-butylammonium buffer solution with isobutyraldehyde solution is so small that pH measurements may not be used to determine the equilibrium constant for imine formation reliably.

Table 15. Summary of Measuring Equilibrium Constant for N-Isobutylidene-3-methoxypropylamine Formation by pH Measurements at 35° C.

$[i\text{-PrCHO}]_o$ M	$[i\text{-PrCOOH}]$ 10^4M	$[RNH_2]_o$ 10^4M	pH of Buffer	Ald. Added ml.	pH	K M^{-1}	K′
0.2137	15.9	298.0	10.388	15.0	10.092	64.1	3520
0.2137	15.9	298.0	10.388	20.0	10.010	65.7	3600
0.2137	15.9	298.0	10.388	25.0	9.942	64.8	3550
0.2137	15.9	298.0	10.388	30.0	9.884	64.9	3550
0.2137	15.9	298.0	10.388	35.0	9.833	64.7	3540
0.2137	15.9	298.0	10.388	40.0	9.792	64.3	3520
0.2137	15.9	298.0	10.388	45.0	9.757	64.5	3530
0.2118	25.4	305.8	10.402	15.0	10.115	62.0	3400
0.2118	25.4	305.8	10.402	20.0	10.036	62.9	3450
0.2118	25.4	305.8	10.402	25.0	9.970	62.4	3420
0.2118	25.4	305.8	10.402	30.0	9.914	62.1	3400
0.2118	25.4	305.8	10.402	35.0	9.867	61.3	3360
0.2118	25.4	305.8	10.402	40.0	9.826	61.1	3340
0.2118	25.4	305.8	10.402	45.0	9.789	60.8	3330
0.2080	55.5	298.6	10.438	15.0	10.150	62.0	3400
0.2080	55.5	298.6	10.438	20.0	10.070	63.5	3480
0.2080	55.5	298.6	10.438	25.0	9.997	65.2	3570
0.2080	55.5	298.6	10.438	30.0	9.940	65.1	3570
0.2080	55.5	298.6	10.438	35.0	9.891	64.6	3540
0.2080	55.5	298.6	10.438	40.0	9.842	66.1	3620
0.2080	55.5	298.6	10.438	45.0	9.799	66.8	3650
					Average	63.8 ± 1.5	3490 ± 80

Ultraviolet Measurements

In general, N-isobutylidenealkylamines are not very stable. Although the equilibrium of imine formation can be established by mixing appropriate concentration of isobutyraldehyde and amine solutions, or by hydrolyzing the N-isobutylidenealkylamine, technically it is more convenient to establish the equilibrium by mixing isobutyraldehyde and amine rather than hydrolyzing isobutylidenealkylamine.

Isobutyraldehyde Solution

In the ultraviolet measurements, the isobutyraldehyde solutions were prepared by the following procedure:

A volumetric flask was 95 per cent filled with nitrogen-saturated water. To the flask was added isobutyraldehyde (known weight), and then water was added to the mark. After it was homogeneous, aliquots of solution were removed by pipet and titrated with standard aqueous sodium hydroxide solution. The concentration of isobutyric acid thus found to be present was taken into account in calculating the concentration of isobutyraldehyde.

Amine Solution

Each amine solution was made up using freshly distilled amine and nitrogen-saturated water. The concentration of methylamine was determined by titrating with standard acid, whereas the concentrations of other amines were calculated from the weight of amine and the volume of solution.

Extinction Coefficient of Isobutyraldehyde

The apparent extinction coefficients of isobutyraldehyde at 35° and 2850 Å and/or 2300 Å were obtained by preparing the appropriate

concentration of isobutyraldehyde solution and examining the ultraviolet spectra at these particular wavelengths.

The concentration of solutions and optical densities are shown in Table 16. Dividing the optical density by concentration, the extinction coefficient was obtained and listed in the last column of Table 16.

Extinction Coefficients of Amines

Extinction coefficients of the various amines studied in aqueous solution at 35° were determined at some wavelength in the range 2260-2300 Å with the results shown in Tables 17 through 20. The N-isobutylidenemethylamine solutions were found to absorb negligibly at 2850 Å.

Extinction Coefficient of N-Isobutylidenealkylamines

The extinction coefficients of N-isobutylidenealkylamines at their absorption maxima are much greater than those of the corresponding aldehyde or amine at any wavelength in the range in which we made measurements. A very dilute isobutyraldehyde solution and concentrated amine solutions were used. The equilibrium is pushed toward imine formation.

Isobutyraldehyde and methylamine solutions were made up with concentrations of 0.04 M and 3 M respectively, and used in preparing the solutions shown in the table on the following page.

The optical density of each solution at 35° and 2265 Å is listed in Table 20. After correcting for the incompleteness of imine formation by using an estimated K value of 90 (the value obtained from pH measurements could have been used), the extinction coefficient of N-isobutylidenemethylamine was obtained as shown in the right column of Table 21.

Soln. No.	Sample Solution: i-PrCHO Conc.M	i-PrCHO Vol. ml.	H_2O ml.	$MeNH_2$ Conc.M	$MeNH_2$ Vol. ml.	Reference Solution: $MeNH_2$ Conc.M	$MeNH_2$ Vol. ml.	H_2O ml.
1	0.04116	10	0	3.0400	25	3.0400	25	10
2	0.04116	10	10	3.0400	15	3.0400	15	20
3	0.04116	10	20	3.0400	5	3.0400	5	30
4	0.03950	10	10	2.9960	15	2.9960	15	20
5	0.03950	10	10	2.9960	15	2.9960	15	20
6	0.03950	10	15	2.9960	10	2.9960	10	25
7	0.03950	10	15	2.9960	10	2.9960	10	25

Solutions of isobutyraldehyde and the other primary amines with the initials concentrations shown in Tables 22, 23, and 24 were made up in a similar fashion and their absorbances measured at 2280 ± 20 Å in water at 35°. The extinction coefficients shown for the imines were calculated by correcting for incompleteness of imine formation, using K values of 76, 64, and 3.5 for the N-isobutylidene-n-propylamine, the N-isobutylidene-3-methoxypropylamine, and the N-isobutylidene-t-butylamine, respectively.

Extinction Coefficient of N-Isobutylidenemethylamine in n-Hexane

A 100 ml. volumetric flask was 90 per cent filled with n-hexane. To the flask was added 0.14 ml. (0.1052 g) of N-isobutylidenemethylamine to make up 100 ml. of 0.01236 M solution. Twenty-five milliliter Erlenmeyer flasks were used to make up the following solutions.

The optical density of each solution was measured at 35° and 2425 Å referred to n-hexane and was listed in Table 25.

Table 16. Extinction Coefficient of Isobutyraldehyde at 35°

Concentration M	Wavelength Å	Optical Density	Extn. Coeff. $cm.^{-1}M^{-1}$	Av.
0.1366	2850	1.985	14.53	14.60
0.1342	2850	1.969	14.67	
0.1557	2300	0.085	0.54	0.54
0.1246	2300	0.068	0.54	

Table 17. Extinction Coefficient of Methylamine at 35° C and 2265 Å.

No.	Concentration M	Optical Density	Extn. Coeff. $cm.^{-1}M^{-1}$
1	0.6446	1.706	2.65
2	0.6016	1.585	2.64
3	0.4297	1.160	2.70
4	0.4281	1.142	2.67
5	0.4280	1.142	2.67
		Average	2.67 ± 0.02

Table 18. Extinction Coefficient of n-Propylamine at 35° C and 2300 Å.

No.	Concentration M	Optical Density	Extn. Coeff. $cm.^{-1}M^{-1}$
1	1.2125	1.370	1.13
2	0.9094	1.180	1.30
3	0.7275	0.920	1.26
4	0.6063	0.770	1.27
5	0.1572	0.192	1.22
6	0.1179	0.150	1.27
7	0.0786	0.100	1.27
8	0.0629	0.082	1.30
		Average	1.25 ± 0.04

Table 19. Extinction Coefficient of 3-Methoxypropylamine at 35° C and 2300 Å

No.	Concentration M	Optical Density	Extn. Coeff. $cm.^{-1}M^{-1}$
1	0.2446	0.272	1.11
2	0.3884	0.448	1.15
3	0.4893	0.500	1.02
4	0.5826	0.600	1.03
5	0.7339	0.730	0.99
6	0.7767	0.770	0.99
7	0.9786	0.934	0.95
		Average	1.03 ± 0.05

Table 20. Extinction Coefficient of t-Butylamine at 35° C and 2260 Å.

No.	Concentration M	Optical Densities	Extn. Coeff. $cm.^{-1}M^{-1}$
1	0.1177	0.580	4.93
2	0.1181	0.595	5.04
3	0.1766	0.875	4.95
4	0.1772	0.889	5.01
5	0.2354	1.155	4.91
6	0.2362	1.170	4.95
		Average	4.96 ± 0.04

Table 21. Extinction Coefficient of N-Isobutylidenemethylamine at 35° C and 2265 Å.

Solution No.	Optical Density	Extn. Coeff. $cm.^{-1}M^{-1}$
1	1.693	144.6
2	1.682	144.9
3	1.680	147.3
4	1.648	147.2
5	1.647	147.2
6	1.638	147.4
7	1.639	147.4
	Average	146.4 ± 0.8

Table 22. Extinction Coefficient of N-Isobutylidene-n-propylamine at 35° C and 2300 Å.

No.	[i-PrCHO] M	[n-PrNH$_2$] M	Optical Density	Extn. Coeff. cm.$^{-1}$M^{-1}
1	0.01099	1.2125	1.720	153.8
2	0.01099	0.9094	1.698	156.6
3	0.01099	0.7275	1.680	155.6
			Average	155.3 ± 0.7

Table 23. Extinction Coefficient of N-Isobutylidene-3-methoxypropylamine at 35° C and 2300 Å.

No.	[i-PrCHO] M	[CH$_3$O(CH$_2$)$_3$NH$_2$] M	Optical Density	Extn. Coeff. cm.$^{-1}$M^{-1}
1	0.01693	0.4893	1.923	140.4
2	0.01693	0.7339	1.911	138.1
3	0.01693	0.9786	1.904	136.9
4	0.01246	0.3884	1.357	135.6
5	0.01246	0.5826	1.351	133.5
			Average	136.9 ± 1.9

Table 24. Extinction Coefficient of N-isobutylidene-t-butylamine at 35° C and 2260 Å.

No.	[i-PrCHO] M	[t-BuNH$_2$] M	Optical Density	Extn. Coeff. $cm.^{-1}M^{-1}$
1	0.01495	0.4744	1.505	167.2
2	0.01495	0.7116	1.642	162.5
3	0.01495	0.7116	1.650	163.4
4	0.01495	0.9488	1.775	161.4
5	0.01495	0.9488	1.776	161.4
			Average	163.2 ± 1.7

Table 25. Extinction Coefficient of N-Isobutylidenemethylamine in n-Hexane at 2425 Å and 35° C.

No.	0.01236 M solution, ml.	n-Hexane ml.	Optical Density	Extn. Coeff. $cm.^{-1}M^{-1}$
1	0	10	0.834	67.4
2	0	10	0.845	68.3
3	2	10	0.712	69.1
4	2	10	0.710	68.9
5	4	10	0.605	68.5
6	4	10	0.605	68.5
			Average	68.5 ± 0.4

Extinction Coefficient of N-Isobutylidenealkylamines in 2,2,4-Trimethylpentane

To 2,2,4-trimethylpentane were added freshly distilled N-isobutylidenealkylamines to make up solutions with concentrations shown in Tables 26 through 29. The solution for ultraviolet measurements were made up as shown in each table.

Partial Molar Volume of Methylamine and Isobutyraldehyde

For a 3.0132 M aqueous solution of methylamine, d_4^{35} was found to be 0.9654. Based on this measurement, the partial molar volume of methylamine, 40.75 ml. per mole was calculated. That of water is 18 ml. per mole. Therefore, every mole of methylamine replaces 2.26 moles of water. Similarly, isobutyraldehyde has density, d_4^{35}, of 0.7770, and therefore a molar volume of 92.79 ml.per mole is calculated. It is assumed that the partial molar volume in aqueous solution is the same and therefore that each mole replaces 5.16 moles of water.

Partial Molar Volume of n-Propylamine

The partial molar volume of n-propylamine was calculated from the volume of n-propylamine which were used to make up a solution and the concentration of n-propylamine in the solution. By averaging ten values, a partial molar volume of 83.7 $\pm$ 0.6 ml. per mole was obtained, thus, every mole of n-propylamine replaces 4.65 moles of water.

Partial Molar Volume of 3-methoxypropylamine

The partial molar volume of 3-methoxypropylamine is 102.0 $\pm$ 0.2 ml. per mole which is calculated from the volume of pure 3-methoxypropylamine used, the total volume of solution and molarity of eighteen 3-methoxypropylamine solutions. Each mole of 3-methoxypropylamine would replace 5.66 moles of water.

Table 26. Extinction Coefficient of N-Isobutylidenemethylamine in 2,2,4-Trimethylpentane at 2425 Å and 35° C.

No.	0.01272 M Solution, ml.	i-Octane ml.	Optical Density	Extn. Coeff. $cm.^{-1}M^{-1}$
1	0	10	0.858	67.5
2	0	10	0.860	67.6
3	2	10	0.712	67.2
4	2	10	0.712	67.2
5	4	10	0.598	65.9
6	4	10	0.602	66.3
			Average	67.0 ± 0.5

Table 27. Extinction Coefficient of N-Isobutylidene-n-propylamine in 2,2,4-Trimethylpentane at 2450 Å and 35° C.

No.	0.03113 M Solution, ml.	i-Octane ml.	Optical Density	Extn. Coeff. $cm.^{-1}M^{-1}$
1	1.0	2.0	1.730	90.4
2	2.0	1.0	0.870	90.9
3	2.3	0.7	0.622	92.9
			Average	91.4 ± 0.1

Table 28. Extinction Coefficient of N-Isobutylidene-3-methoxypropylamine in 2,2,4-trimethylpentane at 2450 Å and 35°C.

No.	0.03113 M Solution, ml.	i-Octane ml.	Optical Density	Extn. Coeff. $cm^{-1}M^{-1}$
1	1.0	2.0	1.872	90.2
2	2.0	1.0	0.942	90.8
3	1.5	0.5	0.700	90.0
			Average	90.3 ± 0.3

Table 29. Extinction Coefficient of N-Isobutylidene-t-butylamine in 2,2,4-Trimethylpentane at 2500 Å and 35° C.

No.	0.01921 M Solution, ml.	i-Octane ml.	Optical Density	Extn. Coeff. $cm^{-1}M^{-1}$
1	0	3.0	1.625	84.6
2	1.0	2.0	1.070	83.5
3	2.0	1.0	0.542	84.6
			Average	84.2 ± 0.5

Partial Molar Volume of t-Butylamine

The partial molar volume of t-butylamine, 105.7 ± 0.4 ml. per mole was calculated from data on siz t-butylamine solutions, which had concentrations from 0.04 to 1.42 M. By dividing by the molecular weight of water, it may be seen that every mole of t-butylamine replaces 5.87 moles of water.

The Ultraviolet Absorption of Equilibrium Solutions at the Absorption Maximum of N-Isobutylidenemethylamine

The isobutyraldehyde solutions were made up with the concentration of 0.039 M in a 250 ml. volumetric flask. The concentration of free acid present in this solution was determined by titrating with standard sodium hydroxide solution. The solution of 0.07 M methylamine was also prepared in a 250 ml. volumetric flask.

The following solutions were made up in 50 ml. Erlenmeyer flasks for ultraviolet measurements.

	Sample Solution			Reference Solution		Absorbance	
No.	i-PrCHO ml.	H_2O ml.	$MeNH_2$ ml.	H_2O ml.	$MeNH_2$ ml.	I[a]	II[b]
1	10	25	0	35	0	0.006	0.008
2	10	25	0	35	0	0.006	0.010
3	10	23	2	33	2	0.189	-
4	10	21	4	31	4	0.385	-
5	10	20	5	30	5	0.442	0.453
6	10	17	8	27	8	0.616	-
7	10	15	10	25	10	0.727	0.767
8	10	10	15	20	15	0.866	0.940
9	10	5	20	15	20	1.018	1.051
10	10	0	25	10	25	1.094	1.140
Equilibrium Constant			K			95.4	88.0
			K′			5260	4850

[a] Initial concentrations of isobutyraldehyde, isobutyric acid, and methylamine were 0.03924, 2.4×10^{-4}, and 0.06858 M, respectively.

[b] Initial concentrations of isobutyraldehyde, isobutyric acid, and methylamine were 0.03965, 1.0×10^{-4}, and 0.07000 M, respectively.

The optical density, D, for each solution listed in the last column of the above Table was obtained after the solution had thermal equilibrium at 35° C. It was determined by fixing the spectrophotometer at the wavelength of maximum absorption of N-isobutylidenemethylamine, i.e., 2256 Å. From these two sets of experiments values of K and K′ of 91.7 ± 3.5 and 5050 ± 200 were obtained from Equations (17) and (17′) respectively by the least squares techniques and Burroughs 5000 computer program (Appendix II). The plot of I is shown in Figure 14.

At the Absorption Maximum of Isobutyraldehyde

Isobutyraldehyde and methylamine solutions were prepared with concentrations of 0.06 M and 3 M respectively. The following solution was made up in 25 ml. Erlenmeyer flasks for the ultraviolet measurements.

	Sample Solution			Absorbance	
No.	i-PrCHO ml.	$MeNH_2$ ml.	H_2O ml.	I[a]	II[b]
1	10.00	0	2.00	1.985	1.968
2	10.00	0	2.00	1.985	1.970
3	10.00	0.10	1.90	-	1.655
4	10.00	0.20	1.80	-	1.375
5	10.00	0.25	1.75	1.282	1.190
6	10.00	0.40	1.60	-	0.835
7	10.00	0.50	1.50	0.690	0.637
8	10.00	0.65	1.35	0.470	-
9	10.00	0.70	1.30	-	0.372
10	10.00	0.80	1.20	0.373	-
11	10.00	0.85	1.15	-	0.280
12	10.00	1.00	1.00	0.270	0.243
13	10.00	1.50	0.50	0.179	0.160
14	10.00	2.00	0	0.150	0.120
	Equilibrium Constant		K	88.0	94.0
			K′	4790	5110

[a] Initial concentrations of isobutyraldehyde, isobutyric acid, and methylamine were 0.1640, 25.7 x 10^{-4}, and 2.9750 M, respectively.

[b] Initial concentrations of isobutyraldehyde, isobutyric acid, and methylamine were 0.1610, 17.3 x 10^{-4}, and 3.0100 M, respectively.

Distilled water was used as reference in these measurements. The spectra were measured at 35° C at the absorption maximum of isobutyraldehyde, i.e., 2850 Å. Values of K and K′ of 91.0 ± 3.0 and 4950 ± 160 were obtained from Equations (16) and (16′) respectively. The plot of II is shown in Figure 15.

Ultraviolet Measurements at the Absorption Maximum of N-Ixobutylidenepropylamine

One milliliter of isobutyraldehyde was added to nitrogen-saturated water in a volumetric flask to make 250 ml. of solution. Then 250 ml. of a n-propylamine solution was prepared similarly, using 1.6 ml. of amine. The concentration of isobutyraldehyde and n-propylamine was calculated from their weight respectively.

The following sets of solutions were made up in 50 ml. Erlenmeyer flasks for the ultraviolet measurements.

	Sample Solution			Reference Soln.		Absorbance		
No.	i-PrCHO ml.	H_2O ml.	n-$PrNH_2$ ml.	H_2O ml.	n-$PrNH_2$ ml.	I[a]	II[b]	III[c]
1	10	25	0	35	0	0.002	0.001	0.003
2	10	25	0	35	0	0.000	0.002	0.002
3	10	23	2	33	2	0.230	0.233	0.230
4	10	21	4	31	4	0.460	0.470	0.465
5	10	20	5	30	5	0.540	0.553	0.580
6	10	17	8	27	8	0.778	0.774	0.780
7	10	15	10	25	10	0.880	0.905	0.895
8	10	10	15	20	15	1.102	1.110	1.110
9	10	5	20	15	20	1.230	1.252	1.230
10	10	0	25	10	25	1.302	1.335	1.296
Equilibrium Constant						75.5	77.7	75.8
			K′			4170	4290	4180

[a] Initial concentrations of isobutyraldehyde, isobutyric acid, and n-propylamine were 0.04292, 2.7×10^{-4}, and 0.07680 M, respectively.

[b] Initial concentrations of isobutyraldehyde, isobutyric acid, and n-propylamine were 0.04335, 2.6×10^{-4}, and 0.07731 M, respectively

[c] Initial concentrations of isobutyraldehyde, isobutyric acid, and n-propylamine were 0.04323, 2.6×10^{-4}, and 0.07695 M, respectively.

These measurements were made at 35° C and at the absorption maximum of N-isobutylidenepropylamine, i.e., 2300 Å. Values of K and K′ of 76.3 ± 0.7 and 4210 ± 50 were obtained from Equations (17) and (17′) respectively using the least squares techniques. The plot of I is shown in Figure 16.

The Ultraviolet Absorption of Equilibrium Solutions at the Absorption Maximum of N-isobutylidene-3-methoxypropylamine

Isobutyraldehyde and 3-methoxypropylamine were prepared with concentrations of 0.04 M and 0.079 M respectively. The following solutions were made up in 50 ml. Erlenmeyer flasks for ultraviolet measurements at 35° and 2300 Å.

	Sample Solution			Ref. Solution		Absorbance		
No.	i-PrCHO ml.	H_2O ml.	RNH_2 ml.	H_2O ml.	RNH_2 ml.	I[a]	II[b]	III[c]
1	10	25.0	0	35.0	0	0	0.007	0.008
2	10	25.0	0	35.0	0	0	0.005	0.006
3	10	23.0	2.0	33.0	2.0	0.236	0.222	0.225
4	10	22.5	2.5	32.5	2.5	-	0.282	0.268
5	10	22.0	3.0	32.0	3.0	-	0.330	0.318
6	10	21.0	4.0	31.0	4.0	0.436	0.431	0.420
7	10	20.0	5.0	30.0	5.0	0.528	0.510	0.502
8	10	17.0	8.0	27.0	8.0	0.746	0.712	0.708
9	10	15.0	10.0	25.0	10.0	0.870	0.872	0.882
10	10	10.0	15.0	20.0	15.0	1.058	1.039	1.030
11	10	5.0	20.0	15.0	20.0	1.218	1.170	1.175
12	10	0.0	25.0	10.0	25.0	1.299	-	-
Equilibrium Constant K						69.1	63.1	63.5
			K′			3810	3480	3510

[a]Initial concentrations of isobutyraldehyde, isobutyric acid, and 3-methoxypropylamine were 0.04327, 1.5 x 10^{-4}, and 0.07916 M, respectively.

[b]Initial concentrations of isobutyraldehyde, isobutyric acid, and 3-methoxypropylamine were 0.04350, 0.3 x 10^{-4}, and 0.07926 M, respectively.

[c]Initial concentrations of isobutyraldehyde, isobutyric acid, and 3-methoxypropylamine were 0.04377, 0.3 x 10^{-4}, and 0.07895 M, respectively.

Values of K and K′ of 65.2 ± 2.5 and 3600 ± 140 were obtained from Equations (17) and (17′) respectively. The plot of II is shown in Figure 17.

Ultraviolet Absorption at the Absorption Maximum of N-Isobutylidene-t-butylamine

Isobutyraldehyde and t-butylamine solutions were prepared with concentrations of 0.04 M. and 1.4 M respectively. The following solutions were made up in 50 ml. Erlenmeyer flasks for ultraviolet measurements.

	Sample Solution			Reference Soln.		Absorbance		
No.	i-PrCHO ml.	H_2O ml.	t-$BuNH_2$ ml.	H_2O ml.	t-$BuNH_2$ ml.	I[a]	II[b]	III[c]
1	10	25.0	0	35.0	0	0	0.006	0.002
2	10	25.0	0	35.0	0	0	0.003	0.000
3	10	23.0	2.0	33.0	2.0	0.316	0.303	0.304
4	10	22.5	2.5	32.5	2.5	0.340	0.364	0.348
5	10	22.0	3.0	32.0	3.0	0.391	0.415	0.415
6	10	21.0	4.0	31.0	4.0	0.482	0.490	0.500
7	10	20.0	5.0	30.0	5.0	0.552	0.556	0.530
8	10	17.0	8.0	27.0	8.0	0.708	0.729	0.720
9	10	15.0	10.0	25.0	10.0	0.818	0.840	0.800
10	10	10.0	15.0	20.0	15.0	1.032	1.030	1.046
11	10	5.0	20.0	15.0	20.0	1.162	1.170	1.175
Equilibrium Constant			K			3.62	3.35	3.50
			K′			205	193	199

[a] Initial concentrations of isobutyraldehyde, isobutyric acid, and t-butylamine were 0.04356, 1.7 x 10^{-4}, and 1.4230 M, respectively.

[b] Initial concentrations of isobutyraldehyde, isobutyric acid, and t-butylamine were 0.04342, 1.7 x 10^{-4}, and 1.4191 M, respectively.

[c] Initial concentrations of isobutyraldehyde, isobutyric acid, and t-butylamine were 0.04352, 1.1 x 10^{-4}, and 1.4215 M, respectively.

These measurements were made at 35° C and 2260 Å. Values of K and K′ of 3.49 ± 0.09 and 199 ± 4 were obtained from Equations (17) and (17′) respectively by using the least squares techniques. The plot of II is shown in Figure 18.

Rate of Attainment of Equilibrium in Imine Formation

During the absorbance and pH measurements there was no significant drift in the values obtained, showing that the composition of the solutions were not changing appreciably at this time. In order to assure thermal equilibrium, at least five minutes was allowed to elapse before the equilibrium absorbance values were measured in the spectral determinations of K and at least two minutes was allowed to elapse before equilibrium pH values were measured when K was determined by the pH method.

In one case direct experiments on the reaction rate were made. To a solution of 1.0 ml. 0.0433 M aqueous isobutyraldehyde in 1.0 ml. water, 1.0 ml. of 0.0800 M aqueous n-propylamine solution was added by syringe. The absorbance at 2300 Å increased from 1.238 at 15 sec. to 1.305 where it became constant after about 270 sec. From the extinction coefficients of the aldehyde and amine it may be calculated that the absorbance should have been 0.032 before any reaction occurred. Therefore, the halftime for the reaction under these conditions (room temperature 25-30°) was considerably less than 15 sec. At 35° the reaction should be even more rapid.

These measurements plus the agreement obtained when the equilibrium constant was determined by different methods and in different runs (in some of which the solutions had stood for as much as five minutes before equilibrium measurements were made) using a given method, seem to assure that equilibrium was attained. Further evidence for this point comes from the fact that approximately the same values for K were obtained in measurements in which the imines were

used as the starting material. (These measurements were rendered less reliable by the instability of the imine and by other factors and therefore not reported here.)

Infrared Spectra of N-Isobutylidenealkylamine

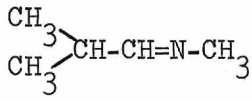
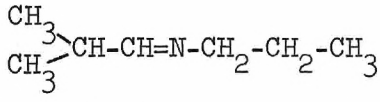
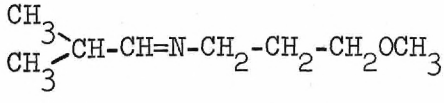
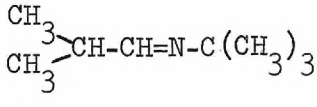
The infrared spectra of N-isobutylidenealkylamines were run in chloroform solution. A 10 ml. volumetric flask was filled with 8 ml. of chloroform, then 0.4 ml. of N-isobutylidenealkylamine was added by syringe. Finally, chloroform was added to the mark. The chloroform solution was run against chloroform by using a pair of 0.1 mm. sodium chloride cells. All four imines studied had an absorption maximum in the range 5.97-6.00 μ, which is attributed to the carbon-nitrogen double bond.

Freshly distilled N-isobutylidenemethylamine was also run neat in a 0.05 mm. sodium chloride cell. The spectrum is shown in Figure 8. After correcting by polystyrene (6.238 μ), the peak for carbon-nitrogen double bond appears at 6.00 μ.

The infrared spectra of N-isobutylidene-n-propylamine, N-isobutylidene-3-methoxypropylamine, and N-isobutylidene-t-butylamine were also run neat in a smear sodium chloride. The spectra are shown in Figures 9-11. After correcting by polystyrene the peak for carbon-nitrogen double bond appear at 5.97, 5.90, and 5.97 μ respectively.

The Nuclear Magnetic Resonance Spectra

The nuclear magnetic resonance spectra are shown in Figures 12-15. The positions of the bands (relative to tetramethylsilane) and some of the coupling constant are assigned as follows:

	Proton	p.p.m.	J.	c.p.s.
	A	1.05		
A B[a] C D	B	2.3	AB	7.0
	C	7.50	BC	4.2
	D	3.16	CD	1.6
	A	1.06	AB	6.8
A B[a] C D E F	B	2.3	BC	4.3
	C	7.48	CD	1.4
	D	3.25	DE	6.4
	E	1.52	EF	6.9
	F	0.82		
	A	1.08	AB	6.9
A B[a] C D E F G	B	2.3	BC	4.2
	C	7.51	CD	1.4
	D	3.41	DE	6.8
	E	1.75	EF	6.3
	F	3.45		
	G	3.21		
	A	1.09	AB	6.9
A B[a] C D	B	2.3	BC	4.1
	C	7.46		
	D	1.15		

[a]The absorption by type B protons was too broad and weak to permit a reliable assignment of the chemical shift, but in all cases it was about 2.3 p.p.m.

CHAPTER V

DISCUSSION

In aqueous solution isobutyraldehyde may be hydrated.

$$(CH_3)_2CHCHO + H_2O \rightleftarrows (CH_3)_2CHCH(OH)_2$$

The hydration of aldehyde is catalyzed by acids; the free acid present can play the role of catalyst. Furthermore, even uncatalyzed hydration proceeds at an appreciable rate.

The extent of hydration of isobutyraldehyde in aqueous solution has been studied by Hine, Houston and Jensen (58) by measurements of the nuclear magnetic resonance spectra. The integrated intensities of the peaks due to the methyl groups of the free aldehyde and hydrate showed that 38 ± 1% of the aldehyde is present as the hydrate at 25° and 30 ± 1% at 35°. These figures correspond to K_h values of 0.0110 and 0.0077 M^{-1}, respectively, where

$$K_h = \frac{[(CH_3)_2CHCH(OH)_2]}{[(CH_3)_2CHCHO][H_2O]}$$

The rate of hydration of isobutyraldehyde has also been studied. The rate constant obtained by Hine and Houston (59) for the acid-catalyzed hydration of isobutyraldehyde in aqueous solution at 35° is 440 ±

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58. J. Hine, J. G. Houston, and J. H. Jensen, J. Org. Chem., 30, 1184 (1965).

59. J. Hine and J. G. Houston, J. Org. Chem., 30, 1328 (1965).

40 $\underline{M}^{-1}$ sec^{-1}.

Due to the presence of the hydrated form of the aldehyde, the extinction coefficient of isobutyraldehyde and equilibrium constant of formation for imines obtained in Chapter IV are the apparent values. They may be corrected for the amounts of hydrated form present to get the true values.

Although the optical density measurements in determinations of the extinction coefficient and equilibrium constant of imine formation were made soon after the solutions were prepared (to minimize the oxidation of isobutyraldehyde and possible complicating reactions of the imine), the rate of hydration is so fast that it would not interfere with the ultraviolet measurements.

The amount of isobutyraldehyde present could be determined by n.m.r. and ultraviolet measurements. The equilibrium constants for aldolization have been determined (57)

$$K_{ald.} = \frac{[(CH_3)_2CHCHOHC(CH_3)_2CHO]}{[(CH_3)_2CHCHO]^2} = 1.05 \pm 0.1 \ \underline{M}^{-1}$$

The purification procedures for isobutyraldehyde did not succeed in removing all of the acid impurities in the aldehyde samples. They may also be formed by oxidation after the aqueous solutions are prepared. In every case we have tried to minimize the amount of free acid.

The apparent extinction coefficient of isobutyraldehyde at 35° is 14.6 $cm.^{-1}\underline{M}^{-1}$. Assuming the isobutyraldol has negligible absorbance and correcting for the amount of the hydrated form, the true extinction coefficient is calculated.

$$\epsilon_{true} = \frac{14.6}{1-0.30} = 20.9 \text{ cm.}^{-1}\underline{M}^{-1}$$

Primary aliphatic aldehydes might give polymeric materials with amines. This is due to the ease with which the imine initially formed undergoes subsequent aldol condensations. For example:

$$(X + 1)R\text{-}CH_2\text{-}CH{=}N\text{-}R' \rightarrow RCH_2\text{-}(CH{=}\overset{R}{\overset{|}{C}})_X\text{-}CH{=}NR$$

Isobutyraldehyde is a secondary aldehyde, which can readily form imines with amines. Fortunately, the fact that this aldehyde has only one α-hydrogen makes the corresponding dimeric imines incapable of splitting out a mole of amine to give an α,β-unsaturated imine which would result in polymerization. Therefore, the complication of polymerization is not involved in the measurement of equilibrium constant of imine formation.

Imine-enamine rearrangement might occur in N-isobutylidenealkylamines but Witkop has shown that the equilibrium in such reactions usually lies well in the side of the imine (60). In calculating the extinction coefficient and equilibrium constant of imine formation, we assume that the amount of enamine present is negligible in all cases.

The ionization constants of the imines are so small that the correction for immonium ion present in equilibration solution is shown to be insignificant.

In the pH measurements, in order to assure that the isobutyraldehyde solution was neutral, the free acid was neutralized by standard

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60. B. Witkop, J. Am. Chem. Soc., 78, 2873 (1956).

sodium hydroxide solution with bromothymol blue as indicator. The ionization constant of bromothymol blue is 10^{-7} (61). The amounts of bromothymol blue being added would not effect the pH value during the measurements to any significant extent. In this measurement it was also assumed that the intermediate (carbinolamine) and product (e.g., imine) would not effect the pH value. The fact that essentially the same equilibrium constants were obtained by the pH method as by spectral measurements, in which ionization of imine would not produce major complications, substantiates this assumption. The pH method may not be used in cases where the equilibrium constants for imine formation are relatively small.

In the ultraviolet measurements, it was assumed that there is no appreciable absorption due to the carbinolamine or its conjugate acids, the ammonium ion, or the imonium ion.

The wavelengths of maximum absorption of N-isobutylidenealkylamines and their extinction coefficients were summarized in the following table.

It can be seen that the wavelengths of absorption maximum shift to higher wavelength from water to 2,2,4-trimethylpentane, whereas the extinction coefficients decrease in hydrocarbon solution. This may be explained due to the usual solvent effect for $n \rightarrow \pi^*$ transitions. The equilibrium constants for imine formation are listed in Table 31.

The equilibrium constant is decreased by the steric hindrance of the R group attached to nitrogen atom of amine. Because only four points are available so far, and these R groups do not have a large

---

61. E. E. Sager, et al., J. Am. Chem. Soc., 73, 732 (1948).

Table 30. Ultraviolet Absorption of Some N-Isobutylidene-alkylamines at 35° C.

$(CH_3)_2CHCH=N-R$		Solvent		
R		Water	i-Octane	n-Hexane
$-CH_3$	λ_{max}(Å)	2265	2425	2425
	ϵ_{max}	146.4	67.0	68.5
$-CH_2CH_2CH_3$	λ_{max}(Å)	2300	2450	
	ϵ_{max}	155.3	91.4	
$-(CH_2)_3OCH_3$	λ_{max}(Å)	2300	2450	
	ϵ_{max}	136.9	90.3	
$-C(CH_3)_3$	λ_{max}(Å)	2260	2500	
	ϵ_{max}	163.2	84.2	

Table 31. Equilibrium Constants for the Formation of N-Isobutylidenealkylamines at 35°.

	UV Measurement		pH Measurement		Average	
	K	K′	K	K′	K	K′
$-CH_3$	91.7 ± 3.5[b]	5050 ± 200[b]	89.5 ± 2.0	4910 ± 90	90.7	4980
$-CH_2CH_2CH_3$	76.3 ± 0.7	4210 ± 50	75.5 ± 1.3	4140 ± 70	75.9	4180
$-(CH_2)_3OCH_3$	65.2 ± 2.5	3600 ± 140	63.8 ± 1.5	3490 ± 80	64.5	3550
$-C(CH_3)_3$	3.5 ± 0.1	199 ± 4	-	-	3.5	199

[a] At the absorption maximum of N-isobutylidenealkylamine.

[b] The value of K and K′ obtained at the absorption maximum of aldehyde are 91.0 ± 3.0 M^{-1} and 4950 ± 160, respectively.

difference in σ^* value, applying the Taft-equation correlation of these data do not give a good straight line.

The dissociation constant of 3-methoxypropylamine does not appear to have been measured. It was obtained by titration of 3-methoxypropylamine with perchloric acid. The pK_b of 3-methoxypropylamine is expected to be in between that of 2-methoxyethylamine, 4.55[4](62), and the unsubstituted primary amine, i.e., n-propylamine, 3.47[5](50). From the results in Figure 4, extrapolated to zero ionic strength, pK_b equal to 3.97 was obtained. Applying the common relation between σ^*_x and $\sigma^*_{xCH_2}$ (63), pK_b equal to 4.10 is estimated from these σ^*'s values, Hall's value for ρ^*(3.14) and log K for primary amines. The extrapolated value, 3.97, is consistent with these predictions.

The band of the proton attached to the imino carbon is at 7.46-7.51 p.p.m. (neat) which is upfield from that of N,N-dipiperonylideneethylenediamine (23) and N-isobutylidenepyrrolidenium ion (24), but is very close to Bonnett's value (7.41-7.50 p.p.m.) (26). The chemical shift of the protons in the methyl groups of the i-propyl group attached to the imino carbon atom are almost the same (1.05-1.09 p.p.m.). The coupling constant of A type protons with B type protons is 6.8-7.0 c.p.s. The coupling constant of vinyl type protons with the one attached to the

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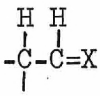
62. R. J. Bruehl, and F. H. Verhoek, J. Am. Chem. Soc., 70, 1401 (1948).

63. J. Hine, Physical Organic Chemistry, 2nd ed., McGraw-Hill Book Company, Inc., New York, 1962, pp.97-98.

[4]This value is at zero ionic strength and 25° C.

[5]This value is at zero ionic strength and 35° C.

carbon atom adjacent to the doubly bonded nitrogen atom is 1.4-1.6 c.p.s. for imines. Thus in system of the type



the coupling constant when X is nitrogen is nearer to that found when X is oxygen (~ 1.3 c.p.s.) than to that found when X is carbon (4-10 c.p.s.) (25).

The nuclear magnetic resonance spectra of N-isobutylidenealkylamines (~ 25%) in chloroform showed that all peaks shift a little bit downfield which indicates that some of the imine molecules form hydrogen bonds in chloroform solution.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The work described in this study has been done with the aim of devising a method to obtain the equilibrium constant for imine formation from isobutyraldehyde and primary alkylamines. Two methods, namely ultraviolet measurements (at absorption maximum of imines and/or aldehyde) and pH measurements, have been proved satisfactory.

Imines and imonium ions are important not only in their own right, but also because they act as intermediates in a wide variety of reactions, such as amine-catalyzed aldolization, decarboxylation, etc. (63).

The following recommendations are made for future, more detailed studies in the present field.

1. Measurement of the equilibrium constant of isobutyraldehyde with ethylamine and isopropylamine. The effect of simple alkyl substituents at the nitrogen atom of N-isobutylidenealkylamine could be obtained from the series methyl, ethyl, i-propyl, and t-butyl groups.

2. Use of primary alkylamines that have strong electron donating or withdrawing groups, such as 2,2,2-trifluoroethylamine, 2-methoxyethylamine, 2-chloroethylamine, or unsaturated alkyl groups which may form a

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64. J. Hine, Physical Organic Chemistry, 2nd ed., McGraw-Hill Book Company, Inc., New York, N.Y., 1962, Secs. 11-3c, 11-4d and 13-1b.

conjugated system with imino double bond. Then, applying these results to Taft-equation correlations, which would make clearer the nature of electronic effects in imine formation.

3. Study of steric effects upon the equilibrium for imine formation. A bulky alkyl group attached to the carbonyl carbon or the nitrogen atom of primary alkyl amines would be expected to decrease the magnitude of equilibrium constant. Thus, the equilibrium constants for ketimines are expected to be smaller than those for the corresponding aldimines. Other kinds of carbonyl compounds (both aldehydes and ketones) and cycloalkylamines (such as cyclopropylamine, cyclobutylamine, cyclohexylamine, etc.) may be used to determine the steric effect in the equilibrium of carbonyl compounds, amines and corresponding imines and/or carbinolamines.

APPENDIX

Table 32. Ionization Constant of Water from 0 to 60° C

t °C.	$K_W \times 10^{14}$	$-\log K_W$
0	0.1139	14.943
5	0.1846	14.734
10	0.2920	14.535
15	0.4505	14.346
20	0.6809	14.167
25	1.008	13.996
30	1.469	13.833
35	2.089	13.680
40	2.919	13.535
45	4.018	13.396
50	5.474	13.262
55	7.297	13.137
60	9.614	13.017

Data from H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions, 3rd ed., Chapter 15, Reinhold Publishing Corp., New York, 1958.

Table 33. Constants of the Debye-Hückel Theory from 0 to 100°.

t °C	(For ion-size parameters, å, in angstrom units) Unit Vol. of Solvent a	b	Unit Wt. of Solvent a	b
0	0.4918	0.3248	0.4918	0.3248
5	0.4952	0.3256	0.4952	0.3256
10	0.4989	0.3264	0.4988	0.3264
15	0.5028	0.3273	0.5026	0.3272
20	0.5070	0.3282	0.5066	0.3279
25	0.5115	0.3291	0.5108	0.3286
30	0.5161	0.3301	0.5150	0.3294
35	0.5211	0.3312	0.5196	0.3302
38	0.5242	0.3318	0.5224	0.3306
40	0.5262	0.3323	0.5242	0.3310
45	0.5317	0.3334	0.5291	0.3318
50	0.5373	0.3346	0.5341	0.3326
55	0.5432	0.3358	0.5393	0.3334
60	0.5494	0.3371	0.5448	0.3343
65	0.5558	0.3384	0.5504	0.3351
70	0.5625	0.3397	0.5562	0.3359
75	0.5695	0.3411	0.5623	0.3368
80	0.5767	0.3426	0.5685	0.3377
85	0.5842	0.3440	0.5750	0.3386
90	0.5920	0.3456	0.5817	0.3396
95	0.6001	0.3471	0.5886	0.3404
100	0.6086	0.3488	0.5958	0.3415

Source: R. A. Robinson and R. H. Stokes, Electrolyte Solutions, 2nd ed., p. 468, Academic Press, New York, 1959. The values for unit weight of solvent were obtained by multiplying the corresponding values for unit volume by the square root of the density of water at the appropriate temperature.

Table 34. Values of (RTln10)/F from 0 to 100°

(ln 10 = 2.30259)

t°C	(RTln10)/F	t°C	(RTln10)/F
0	0.054197	50	0.064118
5	0.055189	55	0.065110
10	0.056181	60	0.066102
15	0.057173	65	0.067094
20	0.058165	70	0.068086
25	0.059157	75	0.069078
30	0.060149	80	0.070070
35	0.061141	85	0.071062
38	0.061737	90	0.072054
40	0.062133	95	0.073046
45	0.063126	100	0.074038

R = 8.3143 joules $deg^{-1} mole^{-1}$; F = 96,487.0 coulombs $equiv^{-1}$; T = t(°C) + 273.150: Report of the National Academy of Sciences-National Research Council Committee on Fundamental Constants, 1963.

APPENDIX

COMPUTER PROGRAM FOR CALCULATION OF EQUILIBRIUM CONSTANTS BY ULTRAVIOLET METHOD*

This program was written in a simplified language prepared by Dr. L. J. Gallagher of the Engineering Experiment Station, Georgia Institute of Technology, especially for the Burroughs B-5000. A special tape of computer instructions is required in order to use this simplified ALGOL language.

COMMENT

N	=	NUMBER OF SOLUTIONS	4	0029
OALD	=	CONCENTRATION OF ALDEHYDE SOLUTION	5	0029
OAM	=	CONCENTRATION OF AMIME SOLUTION	6	0029
D	=	OPTICAL DENSITY	7	0029
EI	=	EXTINCTION COEFFICIENT	8	0029
EA	=	EXTINCTION COEFFICIENT	9	0029
EB	=	EXTINCTION COEFFICIENT	10	0029
P	=	CONCENTRATION OF ISOBUTYRIC ACID	11	0029
KIA	=	IONIZATION CONSTANT OF AMINE	12	0029
K1	=	EQ. CONSTANT BY FIRST APPROXIMATION	13	0029
MA	=	PARTIAL MOLAR VOLUME OF ALDEHYDE	14	0029
MB	=	PARTIAL MOLAR VOLUME OF AMINE	15	0029
VALD	=	VOLUME OF ALDEHYDE IN MIXTURE	16	0029

*We wish to thank Mr. R. F. Ellis for writing this program.

```
COMMENT
VW     =  VOLUME OF WATER IN MIXTURE                          17      0029
VAM    =  VOLUME OF AMINE IN MIXTURE                          18      0029
AO     =  ORIGINAL CONCENTRATION OF ALDEHYDE                  19      0029
BO1    =  ORIGINAL CONCENTRATION OF AMINE                     20      0029
BR     =  FIRST APPROXIMATION OF AMINE REMAINING                      0029
RNH3   =  CONCENTRATION OF AMMONIUM ION                       21      0029
BO     =  CORRECTED ORIGINAL CON. OF AMINE                    22      0029
B      =  FINAL CONCENTRATION OF AMINE                        23      0029
W      =  CONCENTRATION OF WATER                              24      0029
Y      =  AD DEVIDE BY THE DIFFERENCE OF                      25      0029
          OPTICAL DENSITY AND ABS. OF ALD + AM                26      0029
RB     =  RECIPROCAL OF B                                     27      0029
RBW    =  RECIPROCAL OF B TIME W                              28      0029
BEGIN                                                         29      0029
REAL OALD, OAM, P, KIA, K1, EI, EA, EB, MA, MB,               30      0029
                                        START OF SEGMENT ********** 0011
     TINTERCEPT, N, A, J, L:                                  31      0000
ARRAY VALD[1:20], VAM[1:20], VW[1:20], AO[1:20],              32      0000
     BO1[1:20], RNH3[1:20], BO[1:20], B[1:20],                33      0008
     RB[1:20], Y[1:20], W[1:20], RBW[1:20],                   34      0016
     INTERCEPT[1:2], SLOPE[1:2], D[1:20], KEQ[1:2],
       BR[1:20];                                              35      0024
ALPHA ARRAY Z[1:2];                                           36      0034
ALPHA X;                                                      37      0036
```

```
LIST L1(X, N, OALD, OAM, EI, EA, EB, P, KIA, K1,          38        0036
      MA, MB, VALD[1],                                    39        0050
      FOR J←1 STEP 1 UNTIL N DO VW[J], FOR J←1            40        0054
      STEP 1 UNTIL N DO VAM[J], FOR J←1 STEP 1 UNTIL      41        0060
      N DO D[J]);                                      A  41        0066
LIST L2(N, OALD, OAM, EI, EA, EB, P, KIA, K1, MA, MB);    42        0074
LIST L3(J, VALD[J], VW[J], VAM[J], D[J], AO[J], BO1[J],   44        0093
      BR[J], RNH3[J], BO[J], B[J], W[J]);                 45        0109
LIST L4(J,Y[J], RB[J], RBW[J]);                           46        0121
LIST L5(Z[L], INTERCEPT[L], SLOPE[L], KEQ[L]);            47        0133
LIST L6(TINTERCEPT):                                      48        0146
LIST L7(X);                                               49        0152
FORMAT F2(I9,F10.5,F10.5,F9,2,F8.2,F8.2,F11.6,F11.6,      50        0158
                                  START OF SEGMENT ********** 0012
      F10.3,F9.2,F9.2);                                   51        0158
                                  0012 IS 0014 LONG, NEXT SEG 0011
FORMAT F3(I2,F7.1,F7.2,F7.2,F8.3,F10.5,F10.5,F10.5,F11.6            0158
                                  START OF SEGMENT ********** 0013
      F10.5, F10.5,F9.3);                                 53        0158
                                  0013 IS 0015 LONG, NEXT SEG 0011
FORMAT F4(I9,F10.5,F10.3,F11.3);                          54        0158
                                  START OF SEGMENT ********** 0014
                                  0014 IS 0007 LONG, NEXT SEG 0011
FORMAT F5(X7, A6,F12.7,F12.7,F10.3);                      55        0158
```

```
                                        START OF SEGMENT ********** 0015
                                        0015 IS 0008 LONG, NEXT SEG 0011
FORMAT F6(X7,"THEORETICAL INTERCEPT = ",F9.7);          57      0158
                                        START OF SEGMENT ********** 0016
                                        0016 IS 0009 LONG, NEXT SEG 0011
FORMAT F7(X7,A6);                                       58      0158
                                        START OF SEGMENT ********** 0017
                                        0017 IS 0005 LONG, NEXT SEG 0011
      PROCEDURE LEASTSQUARES(Y,X,L):                    82      0158
          VALUE L:                                              0158
            REAL L :                                    83      0158
          ARRAY Y[*], X[*];                             84      0158
          BEGIN                                         85      0158
          REAL   K, SY, SX, SXY, SXSQ:                  83      0158
                                        START OF SEGMENT ********** 0018
          SY←0;                                         86      0000
          FOR K←3 STEP 1 UNTIL N DO SY←SY+Y[K];         87      0000
          SX←0;                                         88      0006
          FOR K←3 STEP 1 UNTIL N DO SX←SY+Y[K];         89      0007
          SXY←0;                                        90      0012
          FOR K←3 STEP 1 UNTIL N DO SXY←SXY+Y[K]xX[K];  91      0013
          SXSQ←0;                                       92      0019
          FOR K←3 STEP 1 UNTIL N DO                     93      0020
          SXSQ←SXSQ+X[K]*2;                             94      0021
          N ← N=2;                                              0025
```

```
        SLOPE[L]←(SXY-(SX×SY)/N)/(SXSQ-SX*2/N);          95      0027
        INTERCEPT[L]←(SY-SLOPE[L]×SX)/N;                 96      0032
        N ← N+2;                                                 0036
        END;                                             97      0037
                                        0018 IS 0040 LONG, NEXT SEG 0011
READFREE(L1,A);                                          62      0158
        PRINT (L1,STANDARD) ; NEWPAGE:                           0159
    FOR J←2 STEP 1 UNTIL N DO VALD[J]←VALD[1];           59      0161
    Z[1]←" Y-1/B";                                       60      0167
    Z[2]←" Y-W/B";                                       61      0169
    TINTERCEPT ← 1/(EI-EA-EB);                           63      0171
    FOR J←1 STEP 1 UNTIL N DO                            64      0173
        BEGIN                                            65      0177
        AO[J]←OALD×(VALD[J]/(VALD[J]+VW[J]+VAM[J]));     66      0177
        BO1[J]←OAM×(VAM[J]/(VALD[J]+VW[J]+VAM[J]));      67      0183
        IF X = "ALDMAX" THEN                                     0190
        BR[J] ← BO1[J] - (AD[J] - D[J]/EA) ELSE                  0191
        BR[J] ← BO1[J] - D[J]/ EI;                               0197
        IF VAM[J]≠0 THEN BEGIN                           68      0203
        RNH3[J]←(+P-KIA+SQRT((-P+KIA)*2+4×KIA×BR
           [J]))/2;                                      69      0205
        BO[J]←BO1[J]- RNH3[J];                           71      0212
        B[J]←(BO[J]-AO[J]-1/K1+SQRT((BO[J]-AO[J]-1/K1)72         0216
           *2+4×BO[J]/K1))/2;                            73      0223
        RB[J]←1/B[J];                                    74      0228
```

```
            IF x = "ALDMAX" THEN                                    76      0231
            Y[J]←AO[J]/((D[1] + D[2])/2 - D[J] + EBx
               BO[J]) ELSE                                          77      0232
            Y[J]←AO[J]/(D[J]-(D[1]+D[2])/2-EBxRNH3[J]);             78      0241
            W[J]←55.176-MAxAO[J]-MBxBO[J];                          79      0251
            RBW[J]←RB[J]xW[J]                                       80      0256
END ELSE    RNH3[J]←BO[J]←B[J]←W[J]←Y[J]←BR[J]←0;                   75      0259
            END;                                                    81      0272
               LEAST SQUARES (Y,RB,1);                              98      0275
               LEAST SQUARES (Y,RBW,2);                             99      0277
        FOR L←1 STEP 1 UNTIL 2 DO KEQ[L]←INTERCEPT[L]/
            SLOPE[L];                                                       0279
         PRINT (L7,F7);                                            100     0287
         SKIPLINE;SKIPLINE;                                        101     0288
         HEADING;SKIPLINE;                                         102     0289
         PRINT (L2,F2);                                            103     0290
         SKIPLINE;SKIPLINE;                                        104     0292
         HEADING;SKIPLINE;                                         105     0293
         FOR J←1 STEP 1 UNTIL N DO PRINT (L3,F3);                  106     0294
         SKIPLINE;SKIPLINE;                                        107     0300
         HEADING;SKIPLINE;                                         108     0301
         FOR J←1 STEP 1 UNTIL N DO PRINT (L4,F4);              A 108     0302
         NEWPAGE;SKIPLINE;SKIPLINE;                                109     0307
         HEADING;SKIPLINE;                                         110     0308
         FOR L←1 STEP 1 UNTIL 2 DO PRINT (L5,F5);                  111     0309
```

```
SKIPLINE;SKIPLINE                                    112      0315
PRINT (L6,F6)                                        113      0316
END;                                                 114      0316

                                    0011 IS 0321 LONG, NEXT SEG 0002
```

The following is an example of input and output. This is one of the data for measuring the equilibrium constant for N-isobutylidene-n-propylamine formation.

AMNMAX

N	OALD	OAM	EI	EA	EB	P	KIA	KI	MA	MB
10	0.04323	0.07695	155.68	0.54	1.25	0.000073	0.000350	75.000	5.16	4.65

	VALD	VW	VAM	D	AO	BO1	BR	RNH3+	BO	B	W
1	10.0	25.00	0.00	0.003	0.01235	0.00000	0.00000	0.000000	0.00000	0.00000	0.000
2	10.0	25.00	0.00	0.002	0.01235	0.00000	0.00000	0.000000	0.00000	0.00000	0.000
3	10.0	23.00	2.00	0.230	0.01235	0.00440	0.00292	0.000882	0.00352	0.00194	55.096
4	10.0	21.00	4.00	0.465	0.01235	0.00879	0.00581	0.001294	0.00750	0.00442	55.077
5	10.0	20.00	5.00	0.580	0.01235	0.01099	0.00727	0.001462	0.00953	0.00579	55.068
6	10.0	17.00	8.00	0.780	0.01235	0.01759	0.01258	0.001964	0.01562	0.01025	55.040
7	10.0	15.00	10.00	0.895	0.01235	0.02199	0.01624	0.002249	0.01974	0.01352	55.020
8	10.0	10.00	15.00	1.110	0.01235	0.03298	0.02585	0.002873	0.03011	0.02237	54.972
9	10.0	5.00	20.00	1.230	0.01235	0.04397	0.03607	0.003417	0.04056	0.03185	54.924
10	10.0	0.00	25.00	1.296	0.01235	0.05497	0.04664	0.003904	0.05106	0.04170	54.875

	Y	RB	RBW
1	0.00000	0.000	0.000
2	0.00000	0.000	0.000
3	0.05456	514.455	28344.371
4	0.02680	226.062	12450.883
5	0.02146	172.690	9509.678
6	0.01594	97.514	5367.133
7	0.01388	73.973	4070.014
8	0.01119	44.706	2457.604
9	0.01010	31.399	1724.521
10	0.00959	23.979	1315.868

	INTERCEPT	SLOPE	EQUILIBRIUM CONSTANT
Y-1/B	0.0069017	0.0000914	75.511
Y-W/B	0.0069120	0.0000017	4167.382

THEORETICAL INTERCEPT = 0.0064981

INFRARED SPECTRA

Polystyrene was used as reference. A pair of 0.05 mm. sodium chloride cells was used for N-isobutylidenemethylamine, and a smear sodium chloride cell was used for the other imines. The instrument was set as follows:

Resolution	= 927	Response	= 2
Gain	= 5	Suppression	= 5
Speed	= 6		

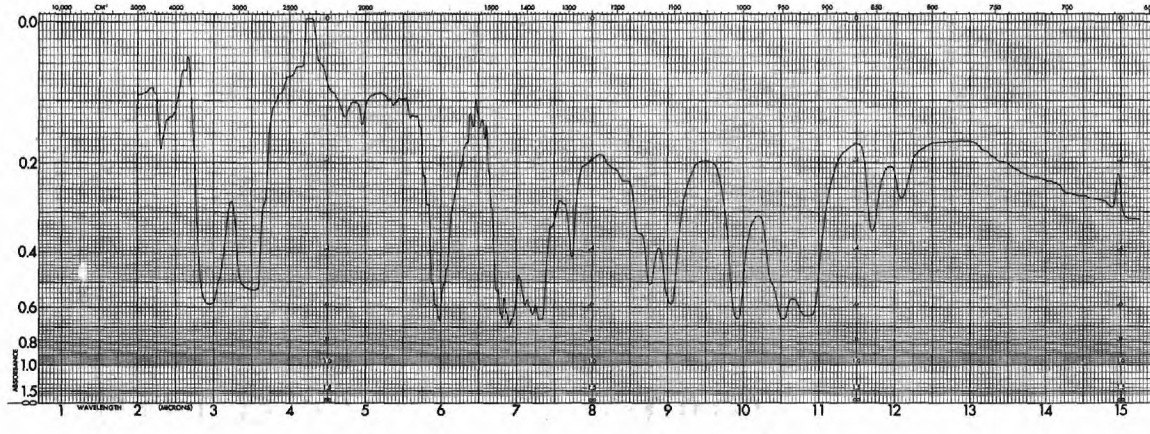

Figure 6. The Infrared Spectrum of N-Isobutylidenemethylamine.

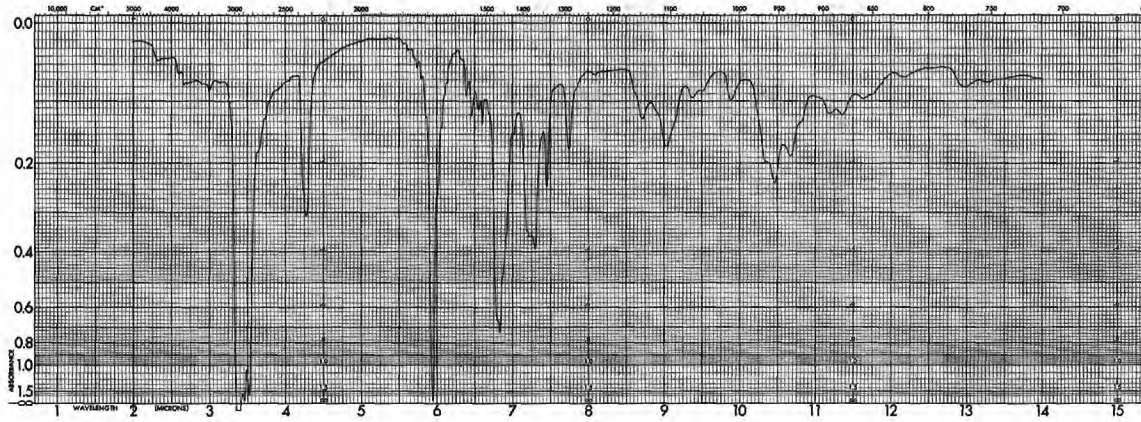

Figure 7. The Infrared Spectrum of N-Isobutylidene-n-propylamine.

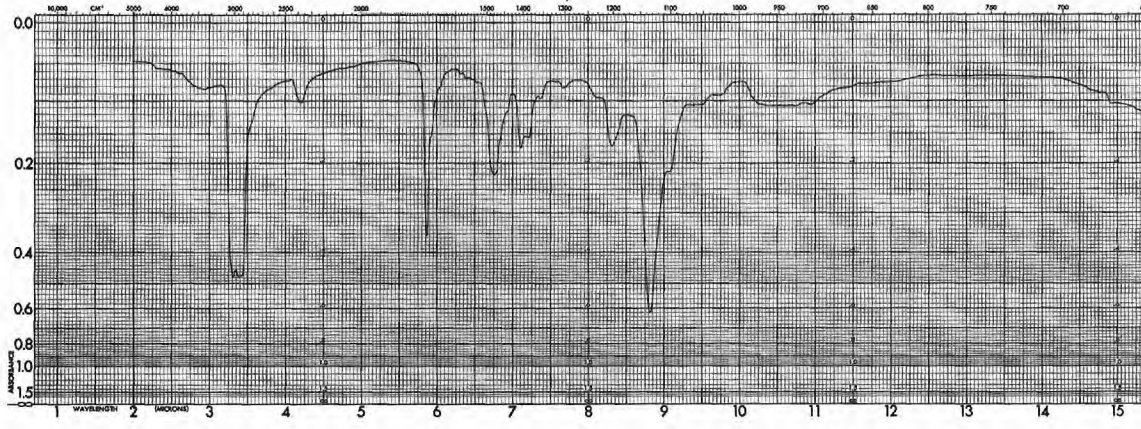

Figure 8. The Infrared Spectrum of N-Isobutylidene-3-methoxypropylamine.

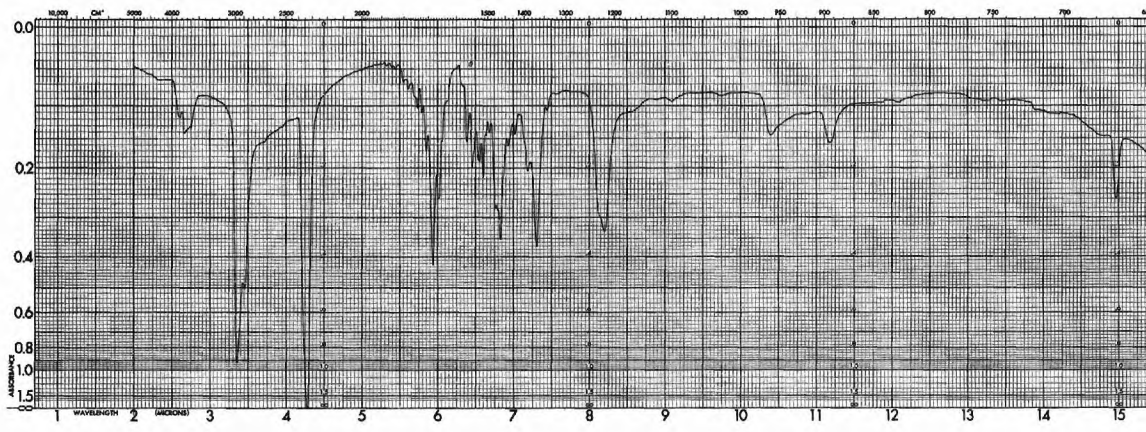

Figure 9. The Infrared Spectrum of N-Isobutylidene-t-butylamine.

NUCLEAR MAGNETIC RESONANCE SPECTRA

Tetramethylsilane was used as an internal reference in the neat spectra. The following abbreviations will be used with the nuclear magnetic resonance spectra:

S.T.	= Sweep Time	R.F.F.	= R.F. Field
S.W.	= Sweep Width	S.O.	= Sweep Offset
F.B.	= Filter Bandwidth	S.A.	= Spectrum Amplitude

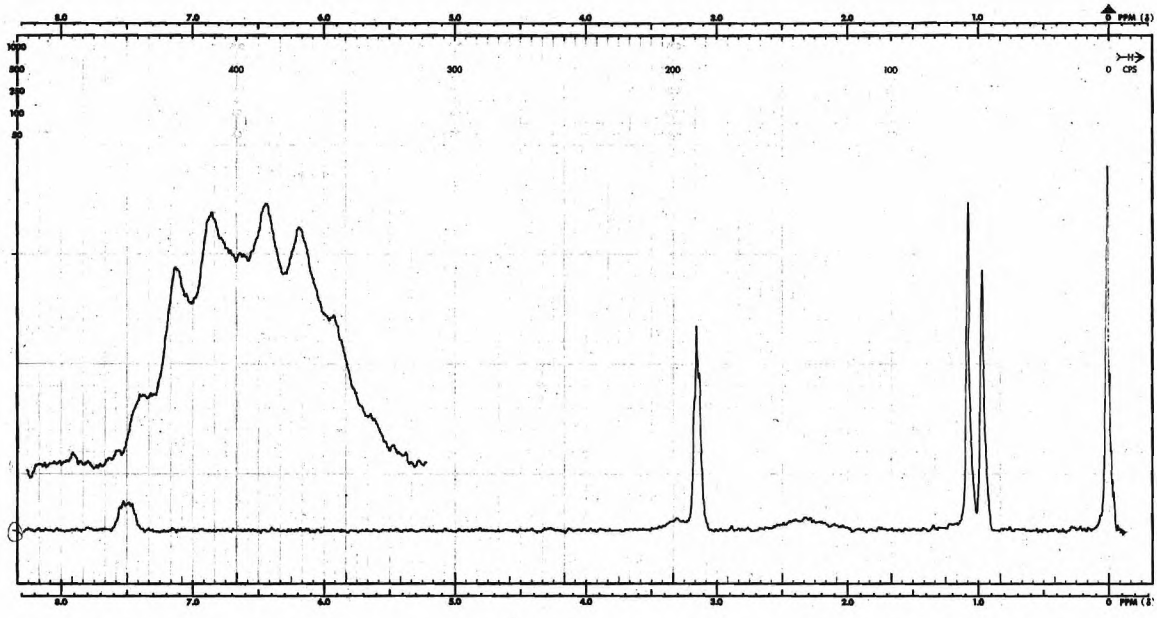

Figure 10. Nuclear Magnetic Resonance Spectrum of N-Isobutylidene-methylamine Neat. F.B.: 2 c.p.s.; R.F.F. 0.10 mG; S.T.: 250 sec.; S.W.: 500 c.p.s.; S.O.: 16 c.p.s.: S.A.: 3.2; Insert F.B. 0.2 c.p.s.; S.W. 50 c.p.s.; S.O.: 418 c.p.s.; S.A.: 40.

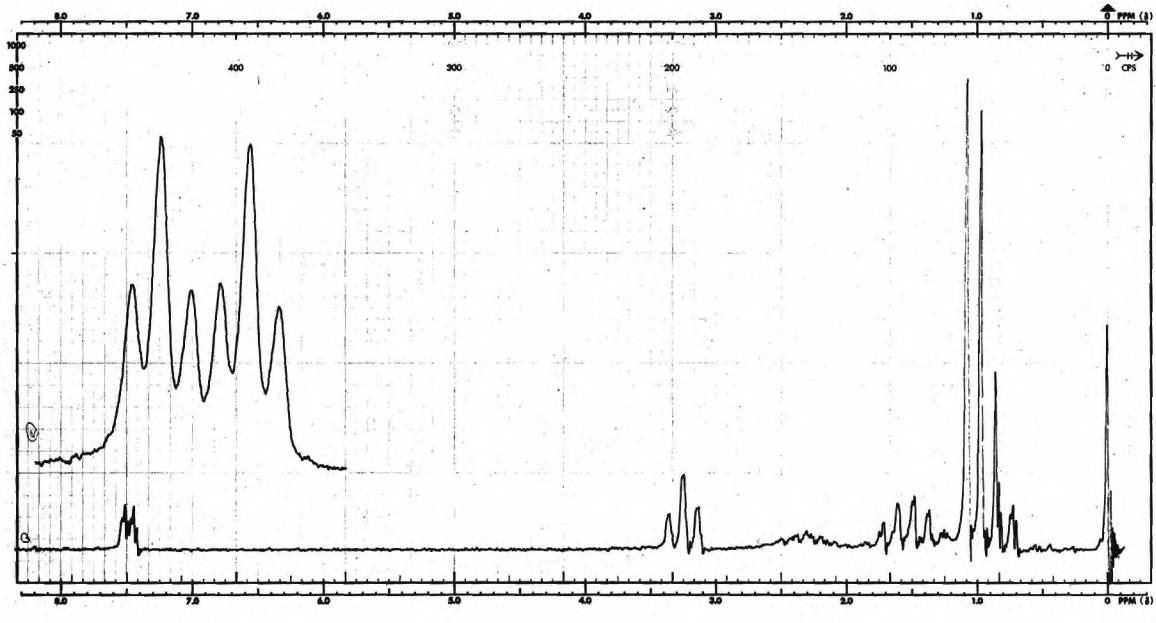

Figure 11. Nuclear Magnetic Resonance Spectrum of N-Isobutylidene-n-propylamine. Neat. F.B.: 2 c.p.s.; R.F.F.: 0.06 mG; S.T.: 250 Sec; S.W.: 500 c.p.s.; S.O.: 24 c.p.s.; S.A.: 1.0; Insert F.B. 0.4 c.p.s.; R.F.F.; 0.10 m.g.; S.W. 50 c.p.s.: S.O. 422 c.p.s.; S.A. 6.3.

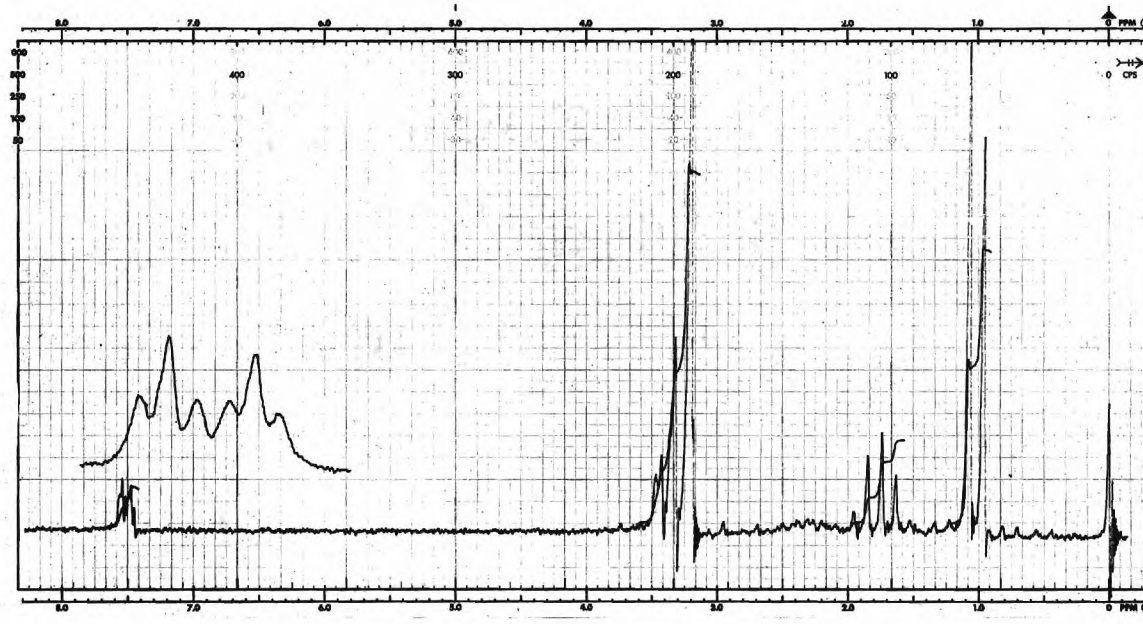

Figure 12. Nuclear Magnetic Resonance Spectrum of N-Isobutylidene-3-methoxypropylamine Neat. F.B.: 4 c.p.s.; R.F.F.: 0.04 mG; S.T.: 250 Sec.; S.W.: 500 c.p.s.; S.O.: 25 c.p.s.; S.A.: 1.0; Insert F.B.: 1 c.p.s.; R.F.F. 0.06 mG; S.W.: 50 c.p.s.; S.O.: 427 c.p.s.; S.A.: 2.5.

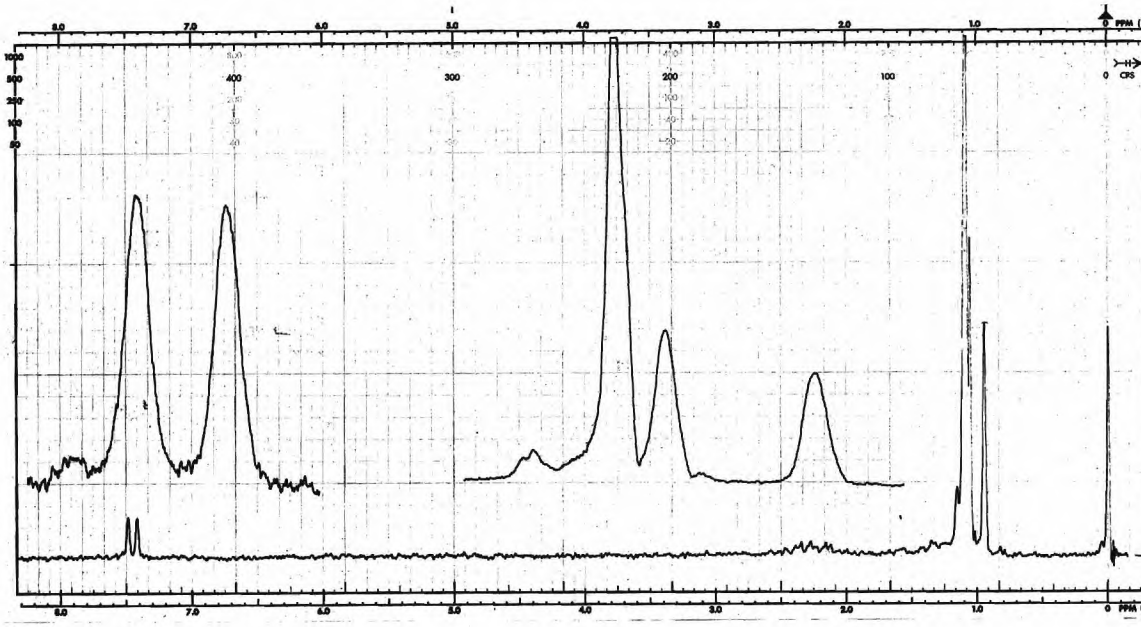

Figure 13. Nuclear Mangetic Resonance Spectrum of N-Isobutylidene-t-butylamine Neat. F.B.: 1 c.p.s.; R.F.F. 0.06 mG; S.T.: 250 Sec.; S.W.: 500 c.p.s.; S.O.: 21; S.A.: 2.5 Insert I.F.B.: 0.4 c.p.s.; R.F.F. 0.10 mG; S.W.: 50 c.p.s.; S.O.: 418 c.p.s.; S.A.: 16. Insert II. F.B. 1 c.p.s.; R.F.F. 0.06; S.W. 50; S.O. 51: S.A. 1.0.

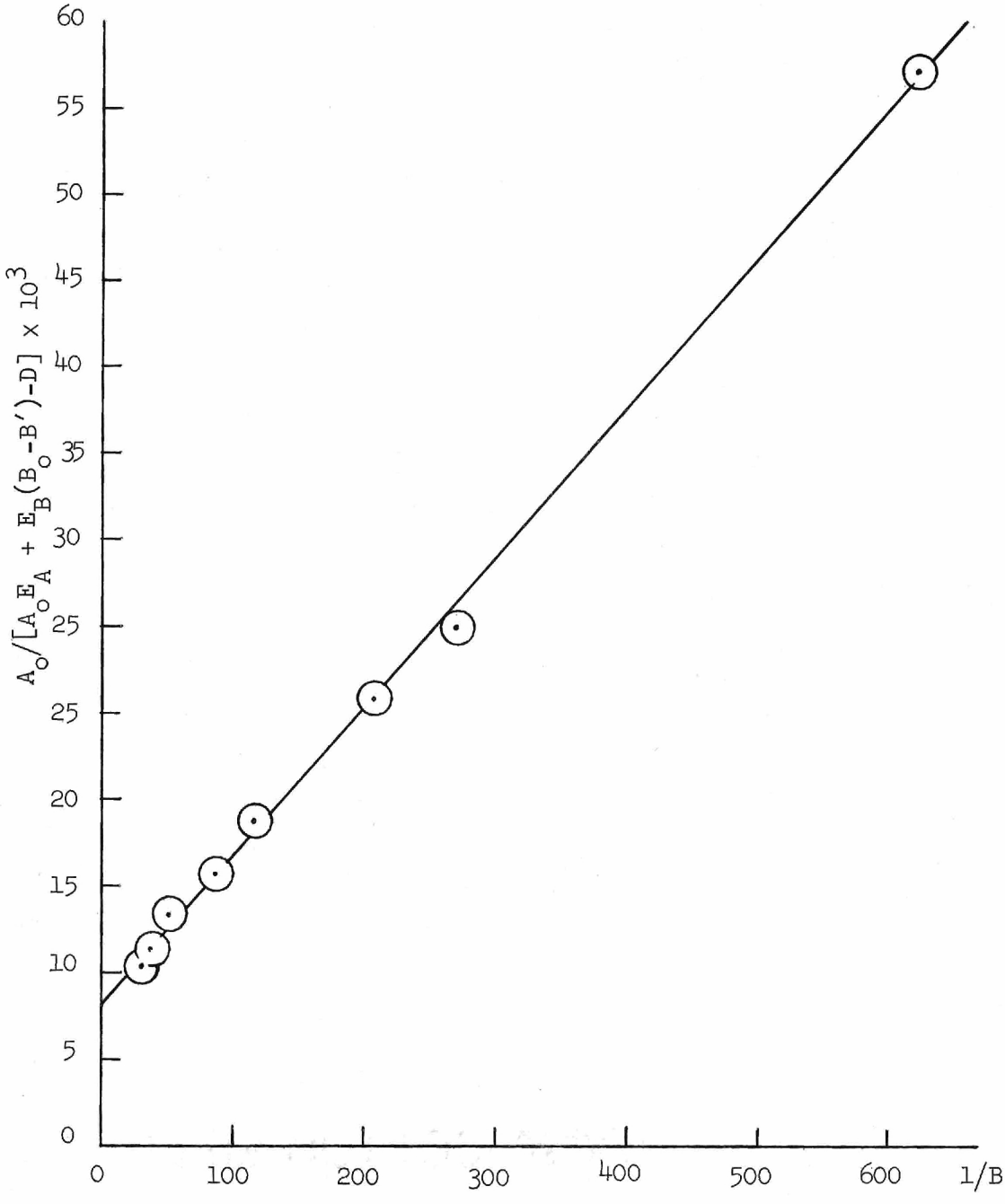

Figure 14. Plot for Determination of Equilibrium Constant for N-Isobutylidenemethylamine Formation by Equation (16).

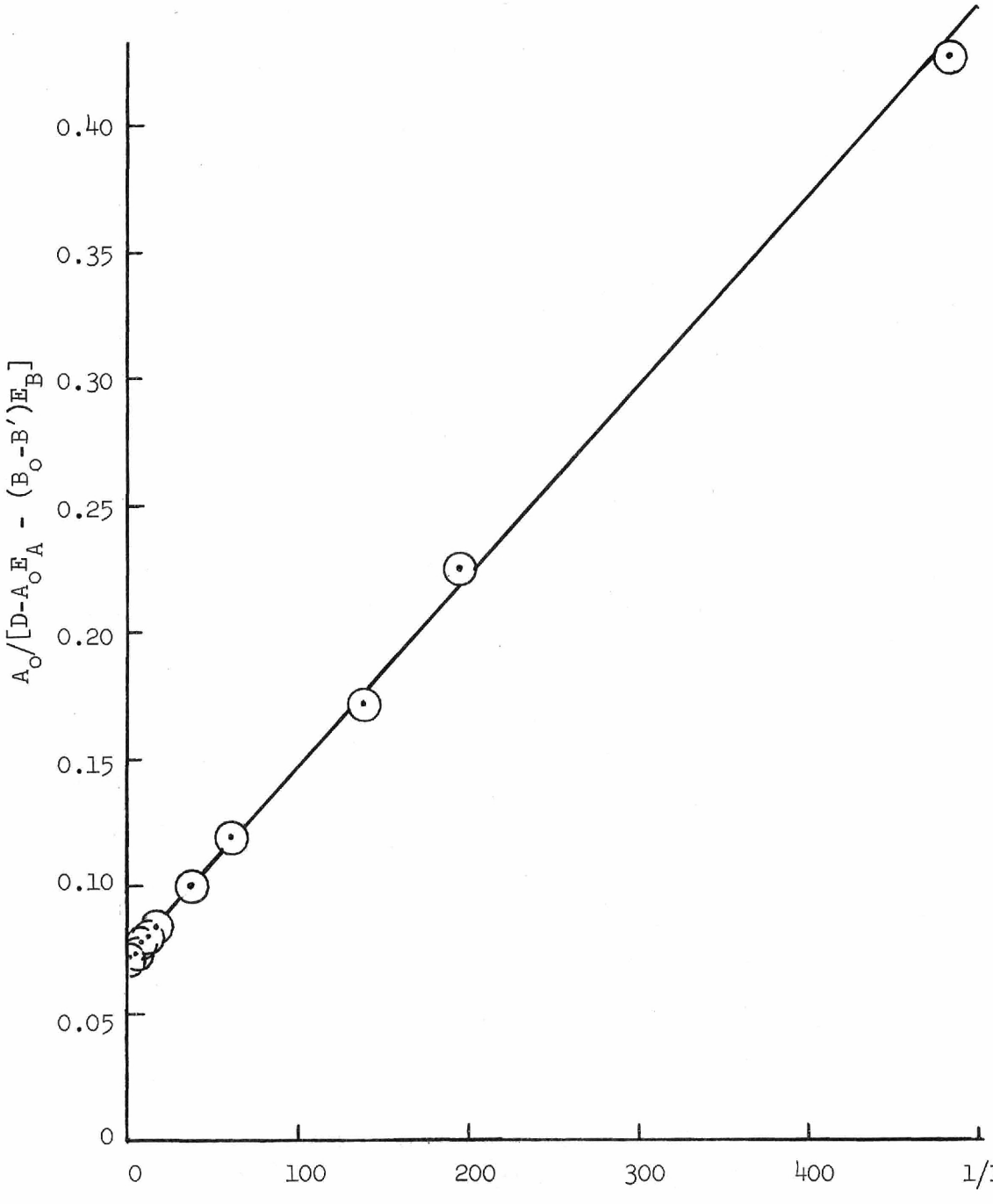

Figure 15. Plot for Determination of Equilibrium Constant for N-Isobutylidenemethylamine Formation by Equation (17).

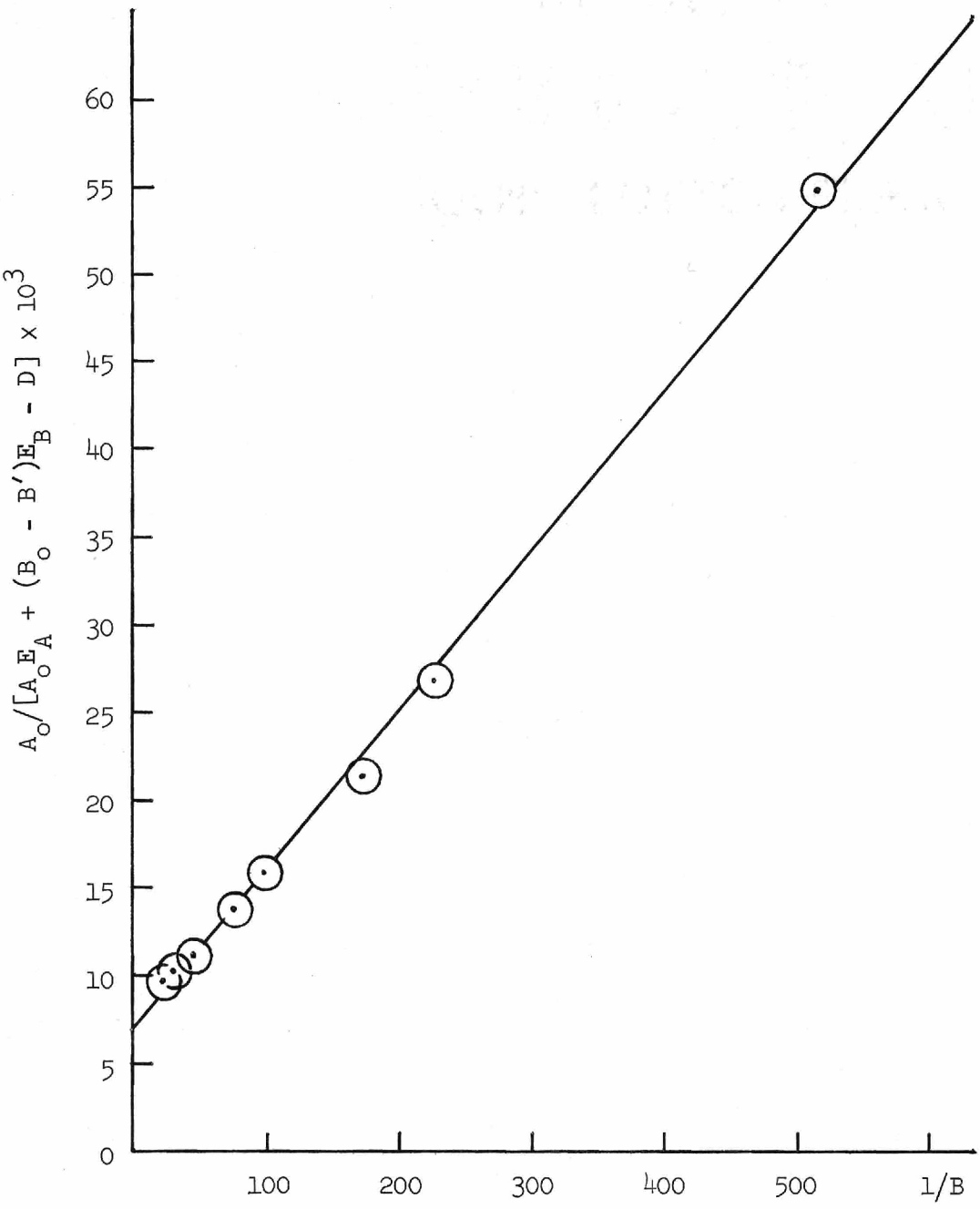

Figure 16. Plot for Determination of Equilibrium Constant for N-Isobutylidene-n-propylamine Formation by Equation (16).

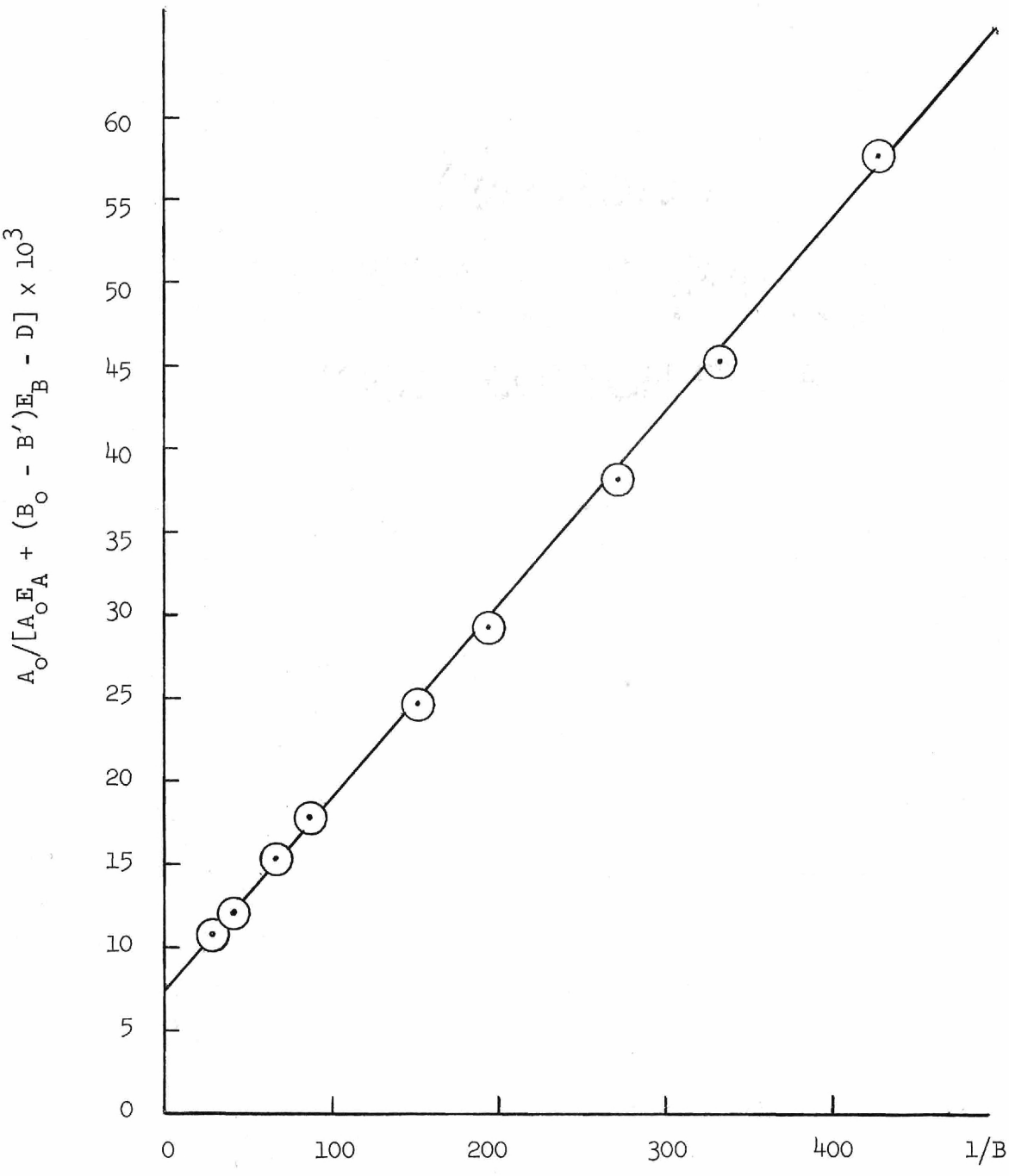

Figure 17. Plot for Determination of Equilibrium Constant for N-Isobutylidene-3-methoxypropylamine Formation by Equation (16).

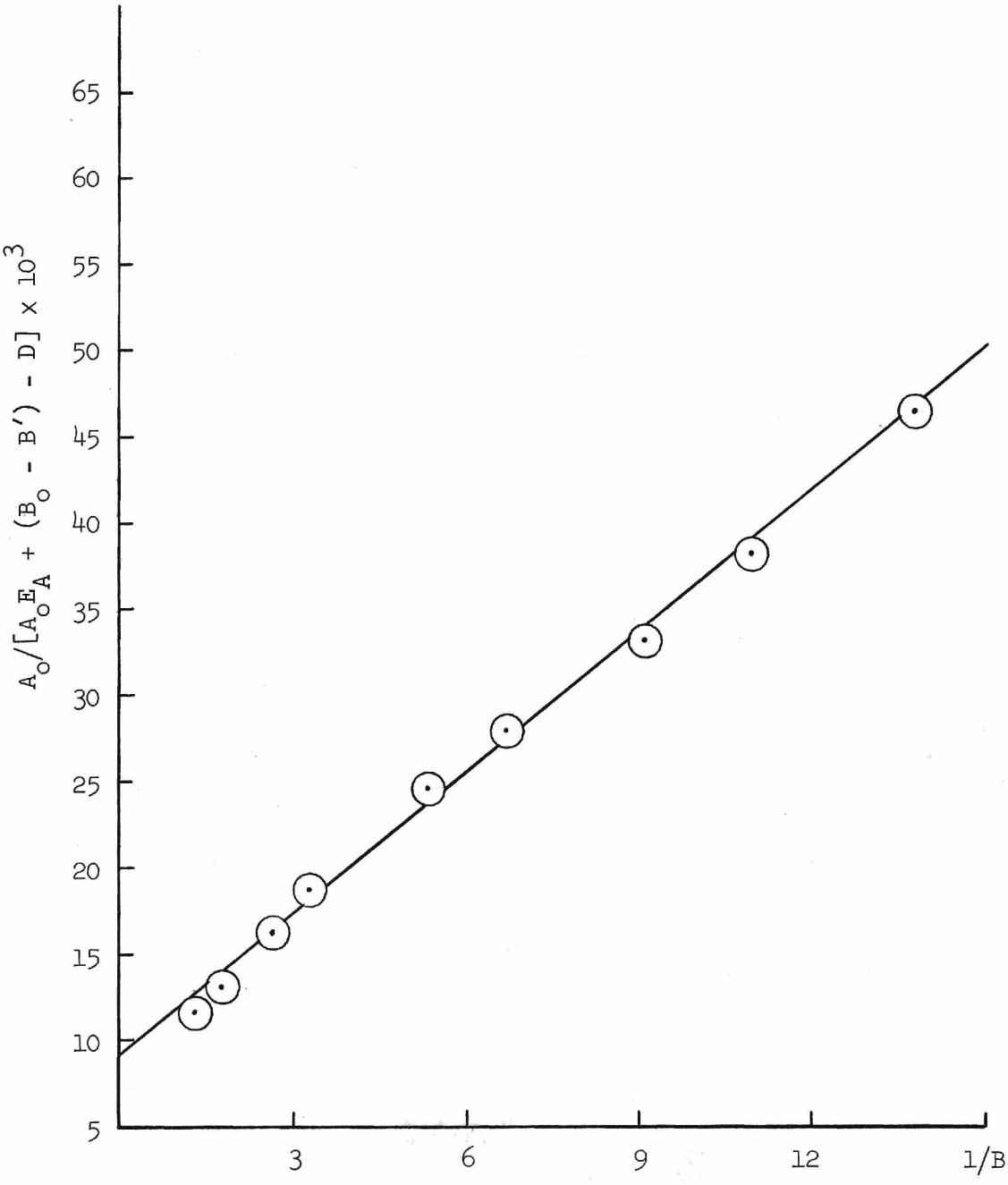

Figure 18. Plot for Determination of Equilibrium Constant for N-Isobutylidene-t-butylamine Formation by Equation (16).

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